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Radii of the Alkali and Halogen Ions and of the Atoms of Inert Gases — WHEELER P. DAVEY 211
Thorium M Series Lines; Critical Potentials — P. A. ROSS 221
Polarization of X-Rays as a Function of Wave-length — PAUL KIRKPATRICK 234
Scattering of X-Rays by Light Elements; a Compressible Quantum Theory — G. E. M. JAUNCEY 239
Scattering of Low Speed Electrons by Pt and Mg — C. DAVISSON AND C. H. KUNSMAN 242
Electrical Conduction; an Equilibrium Theory — A. T. WATERMAN 259
Magnetostriction and Magnetoelectric Effects in Fe, Ni, and Co — PAUL MCCORDLE 271
Measurement of Magnetic Fields of Medium Strength by means of a Magnetron — ALBERT W. HULL 279
Polarization Capacity and Resistance at Radio Frequencies — C. B. JOLLIFFE 293
Acoustical Power of Certain Sound Sources in Absolute Units — PAUL E. SABINE 309

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THE RADII OF THE ALKALI AND HALOGEN IONS AND OF THE ATOMS OF INERT GASES

By Wheeler P. Davey

Abstract

Packing radii of the alkali and halogen ions in crystal lattices.—*An analysis of recent results* for the distances of closest approach of the ions in the lattices of all the alkali halides indicates (1) that these ions pack as though they were nearly spherical in shape; (2) that the heavier ions have packing radii which are nearly constant, i.e. independent of the ions with which they are combined; and (3) that the radii of K^+, Rb^+, and Cs^+ are approximately equal to those of the negative ions with the same number of electrons, Cl^-, Br^-, and I^-, respectively, the approximation being closer the greater the atomic number. Assuming the radii of Cs^+ and I^- to be equal, and that the first two conclusions above hold rigidly, the radii of the ions are computed to be as follows, in units of 10^{-8}cm: for Cs^+ and I^-, 1.974; Rb^+, 1.679; Br^-, 1.737; K^+, 1.548; Cl^-, 1.589; Na^+, 1.1 to 1.2; Fl^-, 1.0 to 1.2. These values are in general agreement with the average of the ionic radii computed by Landé (from crystal data), Richards (from compressibility), and Saha (from ionization potentials), but differ considerably from Bragg's results from x-ray data. The above conclusions are shown to be in qualitative *agreement with the Lewis-Langmuir theory.*

Packing radii of the inert gases computed from x-ray data on the assumption that for each gas the radius is the mean of those for the alkali and halogen ions with the same number of electrons, come out: for Xe, 1.97; Kr, 1.71; Ar, 1.57; Ne, 1.15. These are only from .0 to .27 units higher than the values obtained by Rankine from viscosity measurements. Assuming these radii, the *atomic volume per electron* comes out approximately constant for Xe, Kr and Ne, though somewhat low for Ar.

X-RAY diffraction patterns of crystals not only give the arrangement of atoms in space, but also give in centimeters the distance between the centers of adjacent atoms. These measurements are quite independent of any hypothesis as to the structure of the atoms or of the mechanism of their state of chemical combination.

The results of such measurements on the alkali halides have already been published[1] in detail. A summary is given in Table I for purposes of

[1] Davey, Phys. Rev. 21, 143 (1923).

reference in this paper. The data in this table show two peculiarities. The first has to do with the type of diffraction pattern; the second with certain *differences* in the distance of closest approach. It is the purpose of this paper to discuss these two peculiarities, and to apply the results of the discussion to a determination of the radii of the alkali and halogen ions, and the atoms of the inert gases.

It will be noticed that in the cases of CsI, RbBr and KCl and for these alone, the diffraction pattern and the crystal structure are the same. This means that the component atoms, alkali and halogen, have prac-

TABLE I

Crystallographic data on alkali halides

SC = simple cubic; BCC = Body-centered cubic; FCC = Face-centered cubic

Salt	Diffraction pattern	Crystal structure	Side of unit cube	Distance of closest approach
CsI	BCC	BCC	4.558 A	3.947 ± .004 A
CsBr	SC	BCC	4.287	3.713 ± .004
CsCl	SC	BCC	4.118	3.566 ± .004
CsF	FCC	SC	3.004	3.004 ± .003
RbI	FCC	SC	3.655	3.655 ± .004
RbBr	SC	SC	3.418	3.418 ± .003
RbCl	FCC	SC	3.267	3.267 ± .003
RbF(?)	SC	BCC	3.663	3.172 ± .003
KI	FCC	SC	3.525	3.525 ± .004
KBr	FCC	SC	3.285	3.285 ± .003
KCl	SC	SC	3.138	3.138 ± .003
KF	FCC	SC	2.664	2.664 ± .003
NaI	FCC	SC	3.231	3.231 ± .003
NaBr	FCC	SC	2.968	2.968 ± .003
NaCl	FCC	SC	2.814	2.814 ± .003
NaF	FCC	SC	2.310	2.310 ± .002
LiI	FCC	SC	3.537	*3.537 ± .005
LiBr	FCC	SC	2.745	2.745 ± .003
LiCl	FCC	SC	2.566	2.566 ± .003
LiF	FCC	SC	2.007	2.007 ± .004

* This is quite different from the value of 3.03 ± .01 reported by Posenjak and Wyckoff (J. Wash. Acad. Sci. **12**, 248, 1922). The difference may be due to the method of preparation of the sample. Since Wyckoff's value gives a calculated density more nearly equal to that obtained by ordinary methods, it is reasonable to suppose that his specimen corresponded more nearly to the ordinary state of Li F than my sample did. His value will therefore be used in the calculation of this article.

tically equal diffracting power. The diffracting power is so nearly equal that in the case of KCl additional lines due to incomplete interference could not be found even with prolonged exposures on a photographic film. Now in each of these cases, the atomic numbers differ by only two, so that the positive alkali ions Cs^+, Rb^+ and K^+ have the same number of electrons as the corresponding negative halogen ions, I^-, Br^- and Cl^-. This equality of diffracting power can be readily explained by making

two assumptions, (1) that the elements are present in these compounds, not as neutral atoms, but as electrically charged ions; (2) that the arrangement of electrons in space is the same in Cs^+ as in I^-, in Rb^+ as in Br^- and in K^+ as in Cl^-. The first of these assumptions is consistent with the fact that these compounds are insulators when cold, but become ionic conductors when heated sufficiently. It receives additional support from the refractive equivalents of atoms and ions.[2] The second assumption is necessary in order that groups of equal numbers of electrons may act as equal diffracting centers. It implies equality (or at least approximate equality) in the volumes of Cs^+ and I^-, Rb^+ and Br^-, and K^+ and Cl^-: Although Na^+ and F^- have equal numbers of electrons, their diffracting powers are not quite equal. This is to be expected, because the percentage difference in the nuclear charges is rather great so that the electrons in Na^+ would be expected to occupy a smaller volume than those in F^-. This seems to point to the conclusion that the other pairs of ions mentioned above do not have exactly equal volumes, even though the difference in the space-density of electrons cannot be detected from the type of diffraction pattern. If such is the case, the approximation to equality in volume should be closest in Cs^+ and I^- where the percentage difference in the nuclear charge is least. The same reasons which would make one expect F^- to be a little larger than Na^+ would lead to the conclusion that Cl^- and Br^- should be very slightly larger than K^+ and Rb^+ respectively.

Table II gives the difference in the "distance of closest approach" D of oppositely charged ions in the alkali halides. It will be noticed that within the limits of error, $\pm .007$,

$$D(\mathrm{CsI}) - D(\mathrm{RbI}) = D(\mathrm{CsBr}) - D(\mathrm{RbBr}) = D(\mathrm{CsCl}) - D(\mathrm{RbCl})$$

and

$$D(\mathrm{CsI}) - D(\mathrm{KI}) = D(\mathrm{CsBr}) - D(\mathrm{KBr}) = D(\mathrm{CsCl}) - D(\mathrm{KCl})$$

hence

$$D(\mathrm{CsI}) - D(\mathrm{CsBr}) = D(\mathrm{RbI}) - D(\mathrm{RbBr}) = D\ (\mathrm{KI}) - D(\mathrm{KBr})$$

and

$$D(\mathrm{CsI}) - D\ (\mathrm{CsCl}) = D(\mathrm{RbI}) \neq D(\mathrm{RbCl}) = D(\mathrm{KI}) - D(\mathrm{KCl})$$

These results suggest strongly that each of these ions, Cs^+, Rb^+, K^+, I^-, Br^-, and Cl^- has a dimension, possibly the radius of its "sphere of influence," which we may call its "packing radius" or more simply its "radius," which does not depend on the ion with which it is combined, and that the distance of closest approach is merely the sum of the radii

[2] J. A. Wasastjerna, Oefvers Finska, Vet. Soc. **63** A, 18, (1921); Chem. Abstr. **16**, 3028 (1922).

of the component ions. This is a very surprising result. It is not true for the lightest elements, Na, F, and Li, and this suggests that still more accurate data would show it to be only an approximation for the heavier elements, the approximation being closer the higher the atomic number.

It should be noted that the packing radii are the same when measured along the cube-diagonal (as in the case of the body-centered salts of Cs) as when measured along the cube-edge (as in the case of the simple-cubic salts of Rb and K). This indicates that the ions are approximately

TABLE II

Constancy of size of the large ions

	Iodide	Bromide	Chloride	Fluoride
Cs	3.947	3.713	3.566	3.004
Rb	3.655	3.418	3.267	3.172
Diff.	*.292*	*.295*	*.299*	−.168
Cs	3.947	3.713	3.566	3.004
K	3.525	3.285	3.138	2.664
Diff.	*.422*	*.428*	*.428*	.340
Cs	3.947	3.713	3.566	3.004
Na	3.231	2.968	2.814	2.310
Diff.	.716	.745	.752	.694
Cs	3.947	3.713	3.566	3.004
Li	3.537	2.745	2.566	2.007
Diff.	.410	.968	1.000	.997

	Caesium	Rubidium	Potassium	Sodium	Lithium
I	3.947	3.655	3.525	3.231	3.537
Br	3.713	3.418	3.285	2.968	2.745
Diff.	*.234*	*.237*	*.240*	.263	.792
I	3.947	3.655	3.525	3.231	3.537
Cl	3.566	3.267	3.138	2.814	2.566
Diff.	*.381*	*.388*	*.387*	.417	.971
I	3.947	3.655	3.525	3.231	3.537
F	3.004	3.172	2.664	2.310	2.007
Diff.	.943	.483	.861	.921	1.530

spherical in shape. Other evidence for this conclusion has already been published[3] in which it was shown that these ions pack as though they were cubes with rounded corners, i.e. spheres with six "flat spots." The ions which pack like compressible spheres are those whose electrons do not extend beyond what Langmuir[4] has called the "IIa" layer. As soon as the "IIb" layer is filled the ions act like practically incompressible spheres.

[3] Davey, Phys. Rev. **17**, 402 (1921).

[4] Langmuir, J. Am. Chem. Soc. **41**, 870 (1919).

If we take the distance of closest approach of Cs^+, Rb^+, K^+ to I^-, Br^-, Cl^- as being the sum of the radii of the ions, the experimental results give nine equations. These, together with the four equations given above, give five independent equations containing six unknown quantities. If we assume in addition that $R(Cs^+) = R(I^-)$, which must be very approximately true, as stated above, then we can determine all the radii. The results are given in Table III. It is seen that the radii of Rb^+ and

TABLE III

Radii of the alkali and halogen ions

	Cs+	1.974 A	I−	1.974 A	
	Rb+	1.679	Br−	1.737	
	K+	1.548	Cl−	1.589	
	Na+		F−		Li+
in NaI	1.257 A	in CsF	1.030 A	in LiI**	1.06 A
NaBr	1.231	RbF	(1.493)	in LiBr	1.008
NaCl	1.225	KF	1.116	LiCl	0.977
NaF*	<1.15	NaF*	>1.15	LiF	< 0.86(?)

* As a first approximation, the radii of Na+ and F− are 1.15 A. This is half the distance of closest approach in NaF.

**The radius of Li+ in LiI is 1.563 A if my value is used instead of Wyckoff's.

Br^- and of K^+ and Cl^- are very nearly equal, but that the negative ion is in each case about $\frac{1}{3}$ per cent larger than the positive ion. This is consistent with the prediction made in the first part of this paper. In the case of Na^+, F^- and Li^+, if we assume that the radii of the heavier ions are constant, the radii of the positive ions, Na^+ and Li^+, seem to decrease as the atomic number of the negative ions decreases. The radius of F^- increases as the atomic number of the positive ion decreases. The high value for F^- in RbF seems anomalous.

The Xe atom has the same number of electrons as Cs^+ and I^-. Its nuclear charge lies between that of Cs^+ and that of I^-. It would therefore be expected to have approximately the same radius. In the same way the radius of the Kr atom should be the average of the radii of Rb^+ and Br^-. The radius of Ar should be the average of K^+ and Cl^-, etc. Radii of the atoms of the inert gases, calculated in this way, are given in Table IV. It is also shown in Table IV that these radii are roughly

TABLE IV

Constancy of volume occupied by electrons

Inert Gas	Atomic Number N	$N^{\frac{1}{3}}$	Radius R	$N^{\frac{1}{3}}/R$
Ne	10	2.15	1.15	1.87
Ar	18	2.62	1.57	1.67
Kr	36	3.30	1.71	1.93
Xe	54	3.78	1.97	1.92

proportional to the cube root of the atomic number. That is, *the volume of the atom of an inert gas is roughly proportional to the number of electrons which it contains.* This must mean that the average volume occupied by an electron in an inert gas is approximately a constant. Thus the same conclusion is reached from a study of the diffraction patterns of crystals that was reached by Langmuir[4] from purely chemical considerations.

Table V gives the volume in cubic centimeters of the ions of the alkalies and halogens and of the atoms of the inert gases. The average volume occupied per electron is also given in each case. It is evident that the average volume per electron should be greater for the halogen ions than

TABLE V

Volume occupied by electrons in ions and atoms

Ion or atom	Electrons	Volume (10^{-24}cc)	Volume per electron (10^{-25}cc)
Cs+	54	32.5	6.03
Rb+	36	20.0	5.56
K+	18	15.6	8.67
Na+	10	6.4 to 8.3	6.4 to 8.3
Li+	2	2.6 to 5.0	13 to 25
I−	54	32.5	6.03
Br−	36	22.1	6.14
Cl−	18	17.0	9.44
F−	10	4.6 to 6.4	4.6 to 6.4
Xe	54	32.5	6.03
Kr	36	21.0	5.83
Ar	18	16.3	9.06
Ne	10	6.7	6.7

for the alkali ions, because the attractive force of the nucleus is less. It is not at all certain, however, that these values for the volumes occupied by electrons represent anything more than an *average* for the atoms or ions in question.

In Table VI, the values of the radii of the alkali and halogen ions are compared with the results of other investigators using other methods.[5] The results for the inert gases are compared with the results calculated by Rankine[6] from the viscosity of the inert gases. Since each of these

[5] Landé, Zeit. f. Phys. **1**, 191, (1920);
Richards, J. Am. Chem. Soc. **43**, 1584, (1921); **45**, 422, (1923);
Eve, Nature, **107**, 552 (1921);
Davis, Nat. Acad. Sci. Proc. **8**, 61, (1922);
Saha, Nature, July 28, (1921);
Bragg, Phil. Mag. **40**, 169, (1920);
Pease, J. Am. Chem. Soc. **44**, 769-1497, (1922).

[6] Rankine, Proc. Roy. Soc. **84**, 182, (1910); Phil. Mag. **42**, 601, (1921); Proc. Roy. Soc. **98**, 360, (1922).

methods is founded upon assumptions of one sort or another, it is worth while to examine them further.

Landé assumes that since Li^+ contains only two electrons, it must be negligibly small in the presence of I^- in LiI. If this assumption is correct, the radius of I^- can be at once calculated from the diagonal of the face of the unit cube of LiI. He then tabulates the values for the other ions as the average of the results calculated from the space-lattice constants in terms of the assumed value for iodine. These calculations implicitly assume the constancy of size of I^-. This assumption receives support from Table II of this paper. The space-lattice constants used by Landé were considerably in error. His results have therefore been recalculated for Table VI. In this calculation the side of the unit cube of LiI is taken from Posenjak and Wyckoff's value as given in Table I, since their value gives a calculated density more nearly equal to the commonly accepted value. If my value is used instead, the radii of the negative ions become about 12 per cent larger than given in Table VI

TABLE VI

Comparison of atomic and ionic radii according to various workers

(1) Calculations of Landé; (2) Compressibility method of Richards; (3) Ionization potential method of Eve and Saha; (4) Average of (1), (2) and (3); (5) Viscosity method of Rankine; (6) Crystal structure method of the present article; (7) Crystal structure method of Bragg.

	(1) Landé	(2) Richards	(3) Eve & Saha	(4) Average (1)-(2)-(3)	(5) Rankine	(6) Davey	(7) Bragg
Cs	1.81	2.2*	1.9–	2.0		1.974	2.37
Xe					1.75	1.97	
I	2.14	1.7		1.9		1.974	1.40
Rb	1.51	1.9	1.7	1.7		1.679	2.25
Kr					1.59	1.71	
Br	1.90	1.5		1.7		1.737	1.19
K	1.38	1.6	1.7	1.6		1.548	2.07
Ar					1.43	1.57	
Cl	1.76	1.4		1.6		1.589	1.05
Na	1.09	1.5	1.4	1.3		1.1–1.2	1.77
Ne					1.17	1.15	
F	1.19					1.2–1.0	0.67

* Calculated from CsCl by the writer, using Richards' method.

and the radii of the positive ions become correspondingly smaller. It is not clear that Landé is justified in assuming a negligible radius for Li^+. It is evident, however, that his method must give the upper limits of the radii of the negative ions and the lower limits for the positive ions. These limits could probably be brought closer by using the lattice-constant of HI.

Richards' values depend fundamentally upon his assumption that "the contractions which occur during the formation of the alkali halides are proportional to the compressibilities of the elements concerned." Richards' published value for the radius of Cs^+ is incorrect, due to an error in the method of calculation and the assumption of an incorrect crystal lattice. The value has been recalculated in Table VI. His values of Cs^+ and K^+ do not give differences corresponding to the experimental values of (CsI − KI) or (CsBr − KBr) such as are given in Table II. His fundamental assumption must therefore be regarded as only a good first approximation. The rest of his values check these experimental differences as closely as the accuracy of his end results permits. His values of the halogen ions are all about 10 per cent lower than mine, while his values of the alkali ions are about 10 per cent higher. Richards finds from Bridgman's experimental data that the Na *atom* acts as though it had a relatively incompressible core whose volume is 30 per cent of the volume of the uncompressed atom. It is interesting to note that a similar conclusion can be drawn from the x-ray data. Of the various radii assigned to Na^+ in Table III, the largest (that of Na^+ in NaI) is taken as representing the radius under the smallest compressive force represented in the table, thus corresponding most nearly to the forces used experimentally by Bridgman. This radius is 1.25 A. The radius of the Na atom as determined from the distance of closest approach of atoms in the element[7] is 1.86 A. The volume of Na^+ is therefore .30 of the volume of the Na atom. The close agreement with Richards' value makes it look as though his "relatively incompressible portion" is really the ion. As may be seen from Table II, Na^+ is only "relatively incompressible." It would be valuable if experimental data were available for the pressure volume relations of K, Rb, and Cs. Richards has attempted to fill the gap by extrapolating from the values of Na to those to be expected for K. His extrapolated value for the "incompressible" portion of K is .20 of the value of the atom. The radius of K^+ given in Table IV in comparison with the radius of K,[8] gives a ratio of .33.

A. S. Eve[5] has pointed out, using Bragg's estimate of atomic radii,[5] that the product of the ionization potential by the atomic radius is roughly a constant. M. Saha[5] has used the ionization potentials as a means of calculating atomic radii according to this law. Eve's law holds roughly true with the radii given in Table IV. There is, however, a systematic decrease in the size of the constant as the atomic number decreases. This is to be expected from the fact that the radii are measured at room tem-

[7] A. W. Hull, Phys. Rev. **10**, 661 (1917).
[8] L. W. McKeehan, Proc. Nat. Acad. Sci. **8**, 254 (1922).

perature by the crystal method. The ionization method measures the radius at some higher temperature, probably comparable with that of the boiling point of the element. The correction is in the right direction to reduce the discrepancies in the value of Eve's constant as calculated from the radii given in Table IV. It should be noted that the ionization potentials of the inert gases give radii for the *ions* of the inert gases which are considerably smaller than those assigned for the *atoms* in Table V. This is in accord with theory. The radii as given in this paper do not support B. Davis'[5] modification of Eve's theory in which he claims that the *difference* between the ionization and the radiation potentials, multiplied by the radius, should be a constant.

The best known estimate of radii from crystal data is that of W. L. Bragg.[5] He makes no distinction between the radii of atoms, those of ions, and those of atoms in valence compounds, but apparently he has based all his calculations on "valence compounds." It is inevitable that he should obtain an apparent check between his calculated and observed values, for his number of equations does not exceed the number of his unknown quantities. The values that he gives for the alkalies and halogens do not, however, satisfy the assumption of this article that Cs^+ and I^- have equal radii nor the experimental facts on which that assumption is based. His radii for the alkalies are nearly twice those for the corresponding halogens. In view of the excellent confirmation shown above for the assumption of equality of size it is necessary to reject Bragg's values in so far as ions are concerned. This does not affect in any way the question of the validity of Bragg's radii for atoms which combine to form "valence" compounds.

R. N. Pease[5] has lately estimated the "radii" of atoms in such diamond-like structures as SiC, CuI, AgI, etc., which he considers to be valence compounds, sharing electrons. He finds very good numerical justification for his assumptions. His *radii* for Cl, Br and I do not agree with those given here, nor is there any reason why they should agree if he is correct in assuming that the salts he has considered are "valence compounds."

A. O. Rankine[6] calculated the radii of the atoms of inert gases from his viscosity measurements, using Chapman's formula. Table VI shows that the agreement is not very close. Rankine's results can be converted into mine by the following formula, $(R-0.35)\sqrt{2}=D$ where R stands for Rankine's value for a given radius and D stands for mine. This means that Chapman's formula could be at once modified empirically to give results which correspond with those from the crystal method. So far, I have been unable to find any theoretical reason for such a modi-

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A. S. Eve[5] has pointed out, using Bragg's estimate of atomic radii,[5] that the product of the ionization potential by the atomic radius is roughly a constant. M. Saha[5] has used the ionization potentials as a means of calculating atomic radii according to this law. Eve's law holds roughly true with the radii given in Table IV. There is, however, a systematic decrease in the size of the constant as the atomic number decreases. This is to be expected from the fact that the radii are measured at room tem-

[7] A. W. Hull, Phys. Rev. **10**, 661 (1917).
[8] L. W. McKeehan, Proc. Nat. Acad. Sci. **8**, 254 (1922).

perature by the crystal method. The ionization method measures the radius at some higher temperature, probably comparable with that of the boiling point of the element. The correction is in the right direction to reduce the discrepancies in the value of Eve's constant as calculated from the radii given in Table IV. It should be noted that the ionization potentials of the inert gases give radii for the *ions* of the inert gases which are considerably smaller than those assigned for the *atoms* in Table V. This is in accord with theory. The radii as given in this paper do not support B. Davis'[5] modification of Eve's theory in which he claims that the *difference* between the ionization and the radiation potentials, multiplied by the radius, should be a constant.

The best known estimate of radii from crystal data is that of W. L. Bragg.[5] He makes no distinction between the radii of atoms, those of ions, and those of atoms in valence compounds, but apparently he has based all his calculations on "valence compounds." It is inevitable that he should obtain an apparent check between his calculated and observed values, for his number of equations does not exceed the number of his unknown quantities. The values that he gives for the alkalies and halogens do not, however, satisfy the assumption of this article that Cs^+ and I^- have equal radii nor the experimental facts on which that assumption is based. His radii for the alkalies are nearly twice those for the corresponding halogens. In view of the excellent confirmation shown above for the assumption of equality of size it is necessary to reject Bragg's values in so far as ions are concerned. This does not affect in any way the question of the validity of Bragg's radii for atoms which combine to form "valence" compounds.

R. N. Pease[5] has lately estimated the "radii" of atoms in such diamond-like structures as SiC, CuI, AgI, etc., which he considers to be valence compounds, sharing electrons. He finds very good numerical justification for his assumptions. His *radii* for Cl, Br and I do not agree with those given here, nor is there any reason why they should agree if he is correct in assuming that the salts he has considered are "valence compounds."

A. O. Rankine[6] calculated the radii of the atoms of inert gases from his viscosity measurements, using Chapman's formula. Table VI shows that the agreement is not very close. Rankine's results can be converted into mine by the following formula, $(R-0.35)\sqrt{2}=D$ where R stands for Rankine's value for a given radius and D stands for mine. This means that Chapman's formula could be at once modified empirically to give results which correspond with those from the crystal method. So far, I have been unable to find any theoretical reason for such a modi-

fication. It may be remarked that Rankine's value for Xe falls below the lower limit set by Landé's values, and that his radii do not show constancy of volume occupied by the electrons (see Table V).

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December 2, 1922.

Note added August 27, 1923. R. W. G. Wyckoff, in the Proc. Nat. Acad. Sci. 9, 33 (1923), finds a radius for chlorine of 1.081 A. He arrives at this figure by subtracting the distance between centers of Cs^+ and I^- in CsI from the corresponding distance in $CsCl_2I$. Now $CsCl_2I$ has the Cs and I arranged in a structure like Na^+ and I^- in NaI except that the cube is distorted to a rhombohedron. The Cl atom is at the body-center of this distorted cube. Since the crystal as a whole is electrically neutral, there are three alternatives open: (1) Cs loses an electron to each of the three halogens, so that it has a valence of three; (2) the crystal is made up entirely of uncharged atoms; (3) the Cl is a neutral atom mechanically held in the center of a distorted simple cube of Cs^+ and I^-. Of these three, the last is the simplest and fits best the properties of $CsCl_2I$. If it is correct, Wyckoff's value is not the radius of Cl^- but of the neutral atom of chlorine. The following is evidence of the correctness of this conclusion. Cl^- should be larger than atomic Cl due to the presence of the extra electron, and atomic K should be larger than K^+ in about the same proportion. Assuming that Wyckoff's value applies to atomic Cl we have,

$$Cl/Cl^- = 1.08/1.59 = .68; \qquad K^+/K = 1.55/2.25 = .69.$$

CRITICAL POTENTIALS OF THE THORIUM M SERIES LINES

By P. A. Ross

Abstract

M-series of x-ray lines of thorium.—Spectrograms taken with various potentials decreasing in steps from 10 kv to 3.2 kv, are reproduced which show six lines, α to ϵ of Stenström and a *new line* ϵ_2 of wave-length 2.85 A. By use of screens made of tissue paper soaked in thorium nitrate, five absorption limits, M_1 to M_5, were found, checking the results of Stenström and Coster. The *critical potentials* of the six lines were determined and found to agree with the values predicted by the quantum law from the corresponding absorption limits M_1 to M_5, both δ and ϵ_1 corresponding to M_4, and ϵ_2 to M_5.

Vacuum x-ray spectrograph is described in which a screen with a slit is rotated in front of the plate at twice the angular speed of the crystal so as to prevent scattered rays from striking the plate.

PREVIOUS work on the M series by Karcher,[1] Stenström,[2] and Coster,[3] has been directed toward the determination of the wave-lengths of the lines and of the absorption limits in the x-ray M spectrum. Information as to the source of a particular line has been sought from the

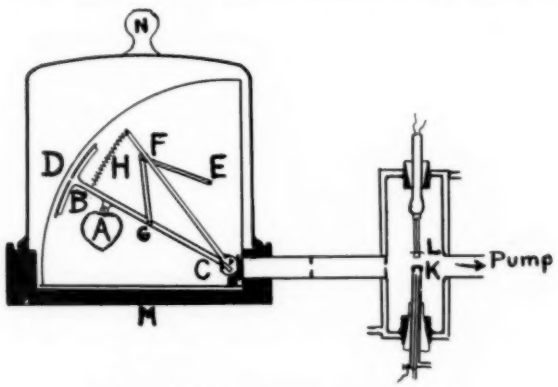

Fig. 1. Vacuum x-ray spectrograph.

law that the frequency of a line is equal to the difference in frequencies of two absorption limits. The relations between lines and limits can probably best be studied by comparison of the critical potentials required

[1] Karcher, Phys. Rev. **15**, 285, 1920.
[2] Stenström, Doc. Dis., Lund, 1919.
[3] Coster, Zeit. fur Phys. **5**, 139, 1921.

to excite the lines with the voltages required to excite general radiation of the frequencies of the absorption limits.

The x-ray tube used in this work was a water cooled brass cylinder with a water-cooled copper target K, Fig. 1, having a thorium button embedded in its face. The target was kindly furnished by the Westing-

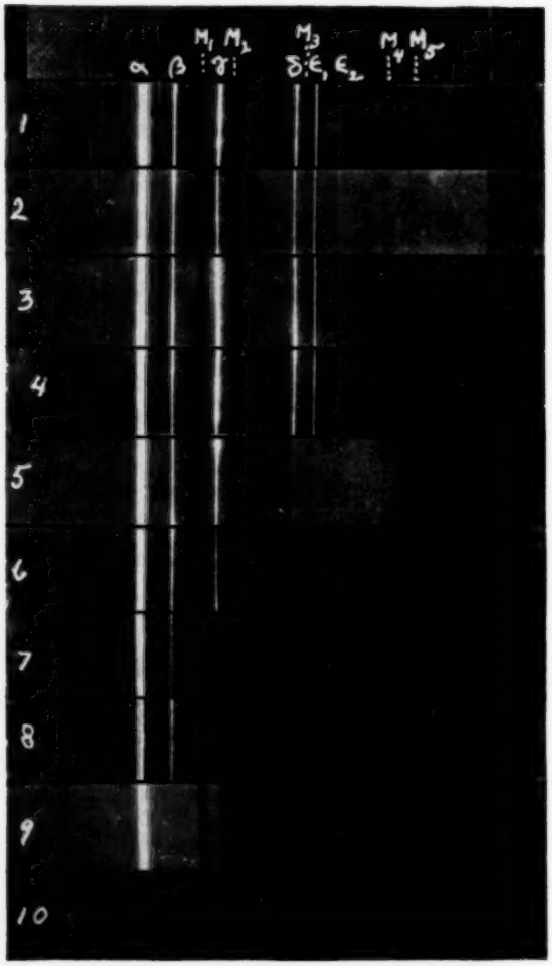

Fig. 2. Spectrograms taken with various potentials decreasing from 10kv to 3.2kv.

house Research Laboratories. The cathode L was a tungsten spiral identical with those used in standard Coolidge tubes. By overheating the spiral, electron currents up to 25 milliamperes could be obtained at from 3 to 5 kv. The direct current at constant voltage was supplied by

the high tension apparatus described elsewhere by D. L. Webster.[4] The x-ray tube was exhausted by means of a diffusion pump kept running constantly. The spectrometer was separated from the x-ray tube by a bit of aluminium foil cemented over the slit at J and was exhausted by the two stage oil-sealed pump supporting the diffusion pump. The spectrometer consisted of a cast iron base *M* with a large glass bell jar *N* of 33 cm inside diameter, ground to a close fit. A little heavy stopcock grease made a sufficiently good seal, though mercury was usually poured in the channel between the foot of the bell jar and the rim of the base. The gypsum crystal at *C* was rotated by means of the arm *F*. The arm *G* carried a screen *B* which served to cut off the scattered radiation, allowing only the regularly reflected beam to pass through a slit *D* at its center. This greatly improved the contrast between lines and background. The arm *F* was made to move with half the angular velocity of *G* by means of the pantograph device *EFG*. *E* is a pivot attached to the brass quadrant carrying the device. At *F* is a sliding contact between the pin and the arm, which is maintained by the light spring *H*. *A* is a cam giving approximately uniform velocity to the arm *BG*. It was driven by means of clock work that gave one oscillation in about six minutes.

For work with the critical potentials it was desirable to reduce the time of exposure as much as possible. This could be done by using the stationary crystal method with the slit system removed and the x-ray tube brought up into direct contact with the iron base.

The absorption spectrum was obtained by using absorption screens made of thin tissue paper soaked in thorium nitrate solution. In Fig. 2, which contains a few typical pictures, the short wave-length limit of the general radiation is shown in all the spectrograms except No. 1. It will be noticed that as the limit of the general radiation passes successive M absorption limits, lines and groups of lines appear. The voltages used were as follows: No. 1, 10 kv; No. 2, 7.8; No. 3, 7.0; No. 4, 5.25; No. 5, 5.02; No. 6, 4.47; No. 7, 4.25; No. 8, 3.83; No. 9, 3.44; No. 10, 3.2. They were measured by an electrostatic voltmeter and checked by the relation $V(\text{in kv}) = 12.345/\lambda$ (in Angstroms) at the limit of the general radiation. The critical voltages recorded below are the average of the lowest measured voltage at which a line appeared and the highest measured voltage at which the line did not appear. Six M series lines corresponding to α, β, γ, δ, and ϵ of Stenström and a new line ϵ_2 of wave-length 2.85 A and five absorption limits were found. Two of the limits, 2.571 A and

[4] Webster, Proc. Nat. Acad. Sci. **6**, 269, May, 1920

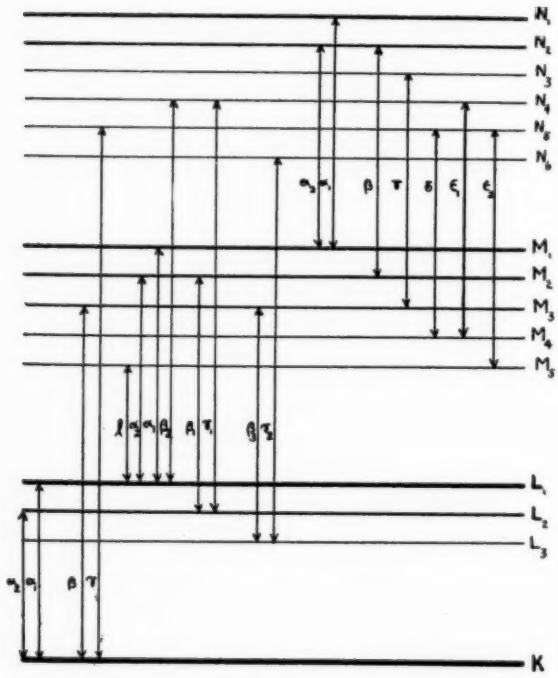

Fig. 3. Relations between M, L and K series.

M					L				
	λ	$\frac{1}{\lambda}$	$\frac{1}{\lambda_{ab_2}}-\frac{1}{\lambda}$			λ	$\frac{1}{\lambda}$	$\frac{1}{\lambda_{ab_2}}-\frac{1}{\lambda}$	
M_1	3.721	.2687			L_1	.7596	1.316		
α	4.1292	.2422	.0265	N_1	l	1.117	.896	.420	M_5
M_2	3.552	.2812			α_2	.969	1.032	.284	M_2
β	3.9333	.2542	.0270	N_2	α_1	.957	1.045	.271	M_1
M_3	3.058	.3269			β_2	.797	1.255	.061	N_4
γ	3.6565	.2736	.0533	N_3	L_2	.6286	1.591		
M_4	2.571	.3889			β_1	.766	1.305	.286	M_2
δ	3.127	.3200	.069	N_5	γ_1	.654	1.530	.061	N_4
ϵ_1	3.006	.3330	.056	N_4	L_3	.6044	1.654		
M_5	2.388	.4188			β_3	.758	1.319	.335	M_3
ϵ_2	2.85	.351	.068	N_5	γ_2	.635	1.575	.079	N_6

K				
	λ	$\frac{1}{\lambda}$	$\frac{1}{\lambda_{ab_2}}-\frac{1}{\lambda}$	
K	.1124	8.889		
α_2	.1368	7.310	1.589	L_2
α_1	.1323	7.559	1.319	L_1
β	.1169	8.559	.330	M_3
γ	.1134	8.820	.079	N_6

2.388 A were not reported by Stenström but have recently been found by Coster.[5] The critical potentials of the lines agree well with the values predicted by the quantum law for the absorption limits M_1, M_2, M_3, M_4, M_5, respectively.

There are faint lines at 4.40 A and at 3.70 A that are possibly due to impurities. The 3.70 line may be the β line of uranium.

Relations between the M, L and K series are summarized in the following table and are also shown graphically in Fig. 3. λ_a refers to the absorption limit. The values in the table are taken from Duane's "Data Relating to X-ray Spectra," National Research Council Bulletin. The values for the K series were computed from Moseley's law $\nu = A(N-b)^2$ plus a correction which was determined by the deviation of the computed K absorption limit from the measured value given by Duane for higher orders than the first, and from the deviation of the computed values of α_2 by Moseley's law from that given by $(K-L_2)$ using measured values of K and L_2. The values of the correction for α_1, β and γ were then obtained by interpolation.

Line	Wave-length in angstroms	Critical voltage	Absorption limit related to line	Product of voltage and limit
α	4.1292	3.3 kv	M_1 3.721	12.25
β	3.9333	3.5	M_2 3.552	12.40
γ	3.6565	4.0	M_3 3.058	12.00
δ	3.127	4.8	M_4 2.571	12.30
ϵ_1	3.006	4.8	M_4 2.571	12.30
ϵ_2	2.85	5.2	M_5 2.388	12.35

STANFORD UNIVERSITY,
March 22, 1923.

[5] Coster, Phys. Rev. **19**, 20, 1922.

POLARIZATION OF X-RAYS AS A FUNCTION OF WAVE-LENGTH

PAUL KIRKPATRICK

ABSTRACT

Polarization of primary x-rays.—(1) *As a function of wave-length.* Rays from a Coolidge target were caused to fall upon a block of paraffin, and the relative intensities of the secondary rays scattered in a plane normal to the primary rays and in directions respectively parallel and perpendicular to the primary cathode rays, were determined by ionization chambers connected to string electrometers. In a qualitative way, the polarization was shown to be greater for the shorter wave-lengths, by the effects of various filters; also the secondary radiation was found more penetrating in the direction of maximum scattering than at right angles. Quantitative results were obtained from the observed changes in the total primary polarization as the form of the spectrum curve was changed in a known manner by the insertion of absorbers in the primary beam. For a maximum voltage of 58 kv, the ratio of components increased from .835 at .3 A to .98 for 1 A. Thus even the shortest wave-lengths (.22A) were not completely polarized. (2) *As a function of voltage*, the mean polarization decreased as the maximum voltage increased from 26 to 64 kv, the corresponding component ratios increasing from .77 to .92. The results indicate that even for a very thin target the polarization would decrease as the cathode ray velocity increased.

INTRODUCTION

KNOWLEDGE of the polarization of primary x-rays dates from the work of Barkla,[1] who showed that when certain substances were struck by x-rays the resulting secondary radiations exhibited maxima and minima of intensity when observed in different directions within a plane normal to the primary beam. This result was shown to imply a polarized condition in the primary beam in such a sense that the predominating component lay in the direction of the cathode stream and of magnitude such that the ratio of the components of polarization equaled the ratio of the intensities of maximum and minimum scattering.

APPARATUS AND OPERATION

A seven inch, medium focus, tungsten target Coolidge tube was so mounted as to be capable of rotation about a horizontal axis normal to the length of the tube and passing through the center of the focal spot. The source of potential was a 2 kw transformer connected with a 1 kw

[1] Barkla, Phil. Trans. Roy. Soc., A, **204**, p. 467, 1905.

motor-generator driven by storage batteries at 100 volts. This equipment, combined with a sensitive galvanometer and special mercury rheostat in the filament circuit, resulted in a very constant operation of the tube. The tube was supplied with flexible leads permitting a rotation of more than 180° without interfering with operation.

At a distance of 50 cm from the target and in a continuation of the axis of rotation, a rectangular block of paraffin some 5 cm thick was mounted. On the axis of rotation of the tube and 25 cm behind the paraffin was an air-filled ionization chamber connected to and supported by a string electrometer. At one side of the paraffin, and in a line extending horizontally from it at right angles to the axis of rotation, was a tubular ionization chamber 43 cm long filled with methyl iodide vapor and directly connected to a second string electrometer similar to the first. The two electrometers with their chambers were connected in parallel to the same box of dry cells.

Circular holes in lead plates between the x-ray tube and the paraffin scatterer limited the beam striking the block to a diameter of about 7 mm. The aperture of the first mentioned ionization chamber was sufficient to receive this entire beam, after passage through the scatterer. The aperture of the second chamber was 1 cm in width and 28 cm distant from the paraffin. Between this window and the paraffin was a lead tube which prevented radiations from entering the window of the chamber except from the direction of the scatterer.

In making a polarization measurement the tube was first brought to constant operation, a lead screen being interposed between the tube and the scatterer. The positions of the strings of the electrometers were read and the screen removed. After an interval of the order of half a minute the screen was replaced and the new string positions read. The sensitivities of the instruments had been adjusted previously so that the displacements of the two strings in a given period were comparable. The x-ray tube was then rotated through ninety degrees and readings repeated. The ratio of the charges simultaneously received by the two electrometers in a given time interval varied with orientation of the x-ray tube. Supposing the first readings above to have been made with the cathode stream horizontal and the second with the cathode stream vertical, then the scattered radiation was found more intense, relatively to that transmitted, in the second case than in the first, and the quotient of these two ratios was taken as the ratio of the component intensities in the primary beam in the directions of minimum and maximum electric intensity.

Experimental Procedure

As there was no record of observations of polarization with tubes of the Coolidge type, the first work was a repetition of Barkla's experiment with such a tube. In the results secured there was nothing to indicate a difference between this tube and the gas filled type as regards polarization. It is impossible to say just what adjustment of the Coolidge tube corresponds to the "medium soft tube" of Barkla and of Bassler; but at a maximum potential of 60 kv, with paraffin as a radiator, polarizations of the expected order, that is, with the components in the ratio of approximately 0.9, were observed.

This work has been guided by the hypothesis that the (non-characteristic) x-rays emitted as a result of a single encounter of any individual cathode electron are highly polarized, and that the relatively low states of polarization observed in the general radiation from a tube result from the non-coincidence of the planes of polarization of the contributing elementary emissions. Such non-coincidence would result from any lack of parallelism in the paths of the impacting electrons.

Now the parallelism of the paths of the electrons before striking the target in the tube used appears to be highly accurate. Fig. 1 is an x-ray pin hole photograph of the focal spot and in it the spiral form of the filament liberating the electrons is clearly represented. However at a slight depth it is certain that the electronic paths possess very

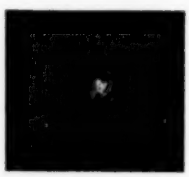

Fig. 1. X-ray pin hole photograph of focal spot on the target.

diverse directions. Maximum polarization would then be expected from surface emissions, with a continuous decrease with depth. This is in conformity with Bassler's[2] observation that polarization decreased with increasing tube hardness, that is with cathode rays of greater penetrating power.

Quantum considerations require that the short wave-lengths of the spectrum originate at or near the target surface and hence they should show greater polarization than the longer wave-lengths, a conclusion

[2] Bassler, Ann. der Phys. **28**, p. 808, 1909.

quite in accord with the observations of Bassler and of Vegard[3] that absorbing substances placed in the primary beam increase its polarization.

The following special experiments confirm the predicted existence and sense of the wave-length variation. Polarization was distinctly increased by filters of copper, lead, or aluminum, which show a uniform increase of absorption with wave-length, but no comparable increase—in cases even a decrease—resulted from the use of filters of silver and of iodine. These substances possess absorption discontinuities within the range of the spectrum employed and hence remove from the beam those wave-lengths which under the present view are taken to be most highly polarized.

The penetrating powers of the two secondary beams from the scattering body were compared by means of absorbers and the beam scattered parallel to the cathode stream was found to be three per cent less penetrating than the normally scattered beam as measured by 0.5 cm of aluminum. This shows that the more highly polarized portion of the spectrum is also the more penetrating portion.

The variation, with generating voltage, of the mean primary polarization was investigated at seven maximum potentials from 25.7 kv to 64.3 kv. The component ratios are plotted against voltage in Fig. 2.

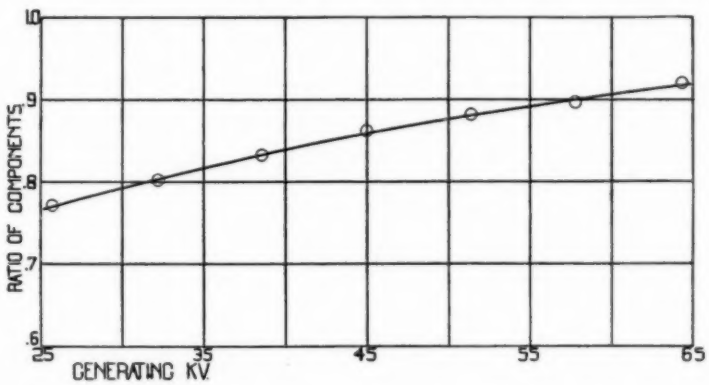

Fig. 2. Variation of the primary polarization with generating voltage.

The curve is concave downwards and indicates that at vanishing penetrations the component ratio would be something less than .5. The curve has the appearance of approaching equality of components asymptotically for higher voltages. With the facilities at hand it was not practicable to extend this curve farther.

[3] Vegard, Proc. Roy. Soc. **83**, p. 379, 1910.

Determination of Polarization as Function of Wave-Length

Having established the variation of polarization with wave-length, it is desirable to secure a quantitative measurement of the wave-length variation. Direct measurement of the polarizations of monochromatic reflected rays was not possible with the available means. However an indirect method was successfully used.

Suppose the form of the continuous spectral energy curve outside the x-ray tube (intensity plotted against wave-length) to be known. From the known absorption coefficients of aluminum one can then construct the form of the spectrum as it will appear after passing through an aluminum filter of any known thickness. The effect of the filter is not merely to reduce the height of the spectrum curve but, on account of the wave-length variation of absorption, to give the curve a new form. By assuming different filter thicknesses let n different spectra be constructed. Then let the polarizations corresponding to each of these n filter thicknesses be actually measured.

The observed polarization has been expressed in this paper by the ratio of the intensity components in the directions of minimum and maximum intensity, which directions may be designated by the letters H and V. Now let the spectrum be divided into n strips each of width $\Delta\lambda$. If P be the measured component ratio for the whole spectrum when no filters are used, and if H_p and V_p be the respective intensities of the H and V components of the pth strip, then

$$P=\frac{\Sigma H_p}{\Sigma V_p}=\frac{H_1+H_2+\ \ldots\ H_n}{V_1+V_2+\ \ldots\ V_n}$$
$$=\frac{H_1+H_2+\ \ldots\ H_n}{E-(H_1+H_2+\ \ldots\ H_n)}$$

E being the total energy of the spectrum. Hence

$$\frac{PE}{1+P}=H_1+H_2+\ \ldots\ H_n.$$

The left member is known, since E is the area under the spectrum curve. In all, n equations of this kind may be written, one for each of the constructed spectra. In all the equations save the one given, the H terms will have coefficients other than unity, determined from the fractional intensity transmitted by the filter used, for the mean wave-length of the strip in question. Thus n simultaneous linear equations in n unknowns result. Their solution gives the H component for each strip, and by comparison with the unfiltered spectrum curve the component ratio for each strip is obtained.

In securing the spectrum curve for carrying out this work, a maximum voltage of 57.9 kv was applied to the tube. A large Bragg spectrometer, rock salt crystal, and methyl iodide chamber were used. Measurements of the intensities at the various wave-lengths were secured by rotating the crystal through the position of reflection and recording the total ionization occasioned. The methods used in correcting the spectrum for the effects of superposed orders, incomplete absorption by the chamber, and variation of crystal reflectivity with wave-length are described in a previous paper.[4]

A solution was secured assuming four spectral strips and employing aluminum filters of thickness 0, .028, .056, .084, .112, .168, .280 cm. Thus seven equations were actually used instead of four in determining the four unknown polarizations. The agreement found among these seven equations is rather remarkable. The average difference between the left members of the equations as originally set up and the left members obtained by inserting back in the equations the values of the unknowns obtained from the solution was .7 per cent. Fig. 3 shows the result graphically. Solutions considering greater numbers of strips than

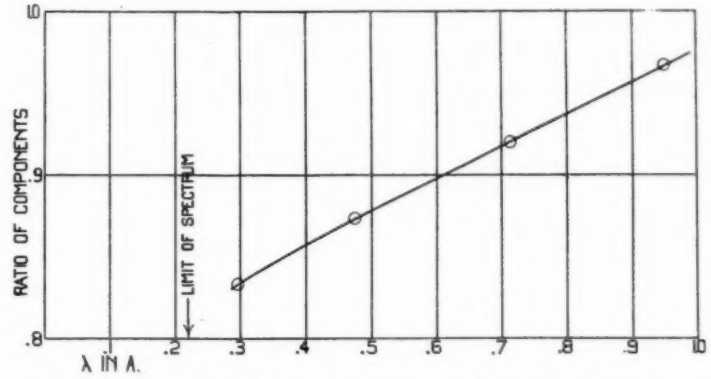

Fig. 3. Polarization as a function of wave-length for x-rays emitted at 58 kv.

four might have been secured, but as the curve turned out to be so nearly linear, such solutions should not alter the form shown to an important extent.

As the minimum wave-length is approached, the polarization is seen to be still far from complete. Even those emissions taking place at the surface of the target, it would appear, must possess a resultant polarization ratio of the order of .8. This result may be taken to mean that the individual emissions though highly or completely polarized possess

[4] Kirkpatrick, Phys. Rev. **22**, p. 37, 1923.

divergent planes of polarization due to the various orientations of the target atoms or the variety of directions of the line of centers of atom and electron at collision. These speculations must wait upon fuller knowledge of the nature of continuous x-ray emission.

Papers upon the scattering of β particles by thin sheets of heavy metals speak of a "change of direction without loss of energy." While this may not be possible in the strictest sense, a close approach to it would explain a low state of polarization quite near to the quantum limit.

Granting that Fig. 3 indicates a component ratio of about 0.8 for target surface emissions at 57.9 maximum kilovolts, another interesting consequence follows. From Fig. 2 it is seen that at 25 kv the average polarization of the entire spectrum gives a component ratio of .765, or lower than that of the shortest wave-length in the 59.7 kv spectrum. Obviously the surface emissions at the lower voltage must possess a lower component ratio than the surface emissions at the higher. The polarization of x-rays from a target so thin that all electron impacts are from the same direction is then a function of the velocity of the electrons.

The writer takes pleasure in acknowledging his indebtedness to Prof. Elmer Dershem for the facilities for this investigation and for advice at many points.

PHYSICAL LABORATORY,
UNIVERSITY OF CALIFORNIA,
January 29, 1923.

A CORPUSCULAR QUANTUM THEORY OF THE SCATTERING OF X-RAYS BY LIGHT ELEMENTS

By G. E. M. Jauncey

Abstract

Corpuscular quantum theory of the scattering of x-rays.—In A. H. Compton's recent theory of the scattering of x-rays in separate quanta, a definite change in wave-length due to scattering is predicted; but in order to calculate the intensity of the scattered beam, he reasons in a not quite rigorous manner from analogy with the Doppler effect. In the present paper it is shown that the energy removed from the primary beam is of the order of magnitude of the energy falling on a sphere of the radius of the electron. It is therefore assumed that quanta of x-rays in the form of corpuscles are deflected by the electrons according to a law of force such that for corpuscles of small momentum (low frequency quanta), the distribution of the scattered rays is that expressed by the classical theory. It is found that for corpuscles of large momentum (high frequency quanta) the scattering electron recoils on collision in such a manner that the distribution of the energy of the scattered rays is modified. Curves and formulas are given showing for different radiation frequencies the theoretical values of the total energy removed from the primary beam by scattering, the energy which reappears in the scattered beam, and the energy of recoil in the scattering electrons. The formula expressing the distribution of the scattered x-rays (Eq. 17) is similiar in form to that obtained by Compton, but gives appreciably different results for very high frequency radiation such as hard γ-rays. Comparison with experimental results for the scattering of hard γ-rays shows an agreement which is probably within experimental error, and which is as good as that obtained with Compton's equations. By slightly modifying the assumptions, however, it is possible to obtain Compton's expression exactly, or to obtain other expressions differing slightly from it.

1. Introduction

IN ORDER to account for the change in wave-length which occurs when a beam of x-rays is scattered, A. H. Compton has proposed the view[1] that each quantum of radiation is scattered by a single electron. The change in momentum of the x-ray, due to its change in direction, results in a recoil of the scattering electron, so that the energy and hence the frequency of the scattered quantum is less than that of the incident ray. The change in wave-length thus predicted is in good accord with the experimental observations. In extending his theory to express the intensity of the radiation scattered in different directions, Compton calculates the intensity of the rays that would be scattered according to

[1] A. H. Compton, Phys. Rev. **21**, 483, 1923.

classical theory if the electrons were moving in the direction of the primary beam at a certain velocity. He takes this velocity as that which, due to the Doppler effect, would give a change in wave-length of the scattered beam equal to that predicted by his quantum theory. While this device gives an expression for the intensity which is in close accord with experiment, the method is not rigorous, as Compton himself points out, since he has not proved that the two scattering processes giving the same wave-length change will necessarily give the same distribution of scattered energy.

In order to avoid the uncertainty of this method of attack, the writer has developed a form of corpuscular quantum theory which does not involve any use of the Doppler effect. This point of view is encouraged by a consideration of the dimensions of the scattering coefficient. According to Thomson's classical theory of x-ray scattering,[2] the energy removed from the primary beam by a single electron is $8\pi e^4 I_0/3m^2c^4$, where e and m are the charge and mass of the electron, c is the velocity of light, and I_0 is the intensity of the incident beam. This is, however, the energy which falls on an area of $(8\pi e^4/3m^2c^4)cm^2$, or on a sphere of $\sqrt{(8/3)}e^2/mc^2 = 4.6 \times 10^{-13}$ cm radius. According to the classical theory, therefore, radiation is scattered as if rebounding from surfaces whose radii are approximately those of the electrons. The problem of x-ray scattering is thus somewhat similar to the scattering of alpha particles by atomic nuclei. This view is similar to that proposed several years ago by W. H. Bragg[3] to explain the asymmetrical distribution of the photo-electrons ejected from matter by x-rays.

If the energy $h\nu$ of a quantum is entirely kinetic, and if the quantum has a momentum $h\nu/c = h/\lambda$, then the quantum cannot be distinguished from a corpuscle except in the matter of frequency. It will accordingly be assumed that the quantum is a corpuscle which in some way gives rise to a frequency expressed by the relation $w = h\nu$, where w is the kinetic energy. Further it will be supposed for the time being that these corpuscles are mathematical points moving with the speed of light. In accord with the considerations of the last paragraph, we must suppose that whenever a corpuscle approaches within a certain distance of the center of an electron it is scattered or deflected. For great wave-lengths, such that the momentum h/λ of the corpuscular ray is small, the mass of the scattering electron is large compared with the effective mass of the quantum, and we may suppose, in accord with experiments, that the scattering is as expressed by the classical theory. But for small wave-

[2] J. J. Thomson, "Conduction of Electricity through Gases," 2nd ed., p. 325.
[3] W. H. Bragg, Nature, Jan. 23, 1908; Phil. Mag. **16**, 918, 1908.

lengths the effective mass of the quantum $h/\lambda c$ approaches that of the electron, and the recoil of the scattering electron after impact with the corpuscular ray, will affect the distribution and the energy of the scattered rays.

2. Scattering of Long Wave-Length X-Rays

In this case an x-ray corpuscle comes within the field of action of the electron and is deflected, the electron having negligible momentum imparted to it, and the corpuscles are scattered to give an energy distribution according to Thomson's classical theory. Let the primary x-rays consist of a beam of corpuscles traveling in a direction parallel to the axis of x. Let there be n_0 corpuscles crossing unit area placed perpendicular to the beam in unit time, so that the intensity of the primary rays is

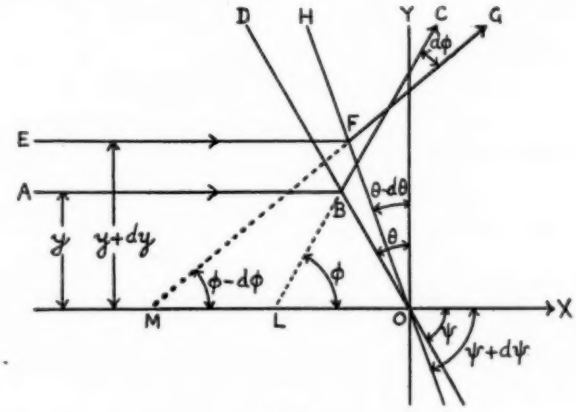

Fig. 1

$n_0 h\nu_0$ ergs/cm² sec. Since in an unpolarized beam of x-rays the scattering is symmetrical about the axis of x, it will be assumed that the field of the electron is symmetrical about this axis. Let the center of the electron be at O on the axis of x in Fig. 1. If the corpuscle approaches the electron along this axis, there is a head-on collision and the corpuscle is scattered directly backwards. If the line of flight of the impinging corpuscle is at a distance y from the x-axis, then the corpuscle is scattered in a direction ϕ, provided that y is not greater than a, where a is the maximum value of y at which scattering takes place. This distance a will be called the "radius" of the electron.

The problem now is to discover the relation between y and ϕ. The number of corpuscles approaching the electron between the perpendicular distances y and $(y+dy)$ is $2\pi n_0 y dy$. These corpuscles are scattered between the angles ϕ and $\phi - d\phi$. Taking a sphere about O as center with

a radius R, where R is very great compared with a, these scattered corpuscles cross an area $-2\pi R^2 \sin\phi d\phi$ on the sphere. The number of corpuscles crossing the sphere per unit area in a direction ϕ is therefore:

$$n_\phi = -\frac{2\pi n_0 y}{2\pi R^2 \sin\phi} \cdot \frac{dy}{d\phi} = -\frac{n_0 y}{R^2 \sin\phi} \cdot \frac{dy}{d\phi} \tag{1}$$

and the intensity of the beam scattered in a direction ϕ is

$$-\frac{n_0 h\nu_0 y}{R^2 \sin\phi} \cdot \frac{dy}{d\phi} = -\frac{I_0 y}{R^2 \sin\phi} \cdot \frac{dy}{d\phi} \tag{2}$$

where I_0 is the intensity of the primary rays. By our hypotheses, this must be equal to the intensity scattered by a single electron according to the classical theory developed by Thomson,[2] i.e.,

$$-\frac{I_0 y}{R^2 \sin\phi} \cdot \frac{dy}{d\phi} = \frac{I_0 e^4}{R^2 m^2 c^4} \cdot \frac{(1+\cos^2\phi)}{2} \tag{3}$$

Integrating this we obtain

$$y^2 = (e^4/3m^2c^4)\ (4+3\ \cos\phi+\cos^3\phi) \tag{4}$$

since $y=0$ when $\phi=180°$. The greatest value of y occurs when $\phi=0$. This is the radius a. Hence

$$a = \sqrt{(8/3)} \times (e^2/mc^2) = 4.57 \times 10^{-13} \text{ cm.} \tag{5}$$

Relation (4) may thus be written

$$y^2 = (a^2/8)\ (4+3\ \cos\phi+\cos^3\phi) \tag{6}$$

Since Thomson's theory is so nearly true for long wave-length x-rays it follows that the radius given in (5) can be taken as the experimental value on the present theory. The total energy scattered by an electron is thus equal to its cross sectional area multiplied by I_0, i.e.,

$$\pi a^2 I_0 = (8\pi/3)\ (e^4/m^2c^4) I_0 \tag{7}$$

This is, as it should be, the same as the total energy scattered by an electron according to Thomson's theory.

3. Scattering of Short Wave-Length X-rays

In Compton's paper the equations expressing the conservation of energy and the conservation of momentum when a quantum is scattered by an electron are, referring to Fig. 2,

$$h\nu_0 - h\nu_\phi = [(1-\beta^2)^{-\frac{1}{2}} - 1]mc^2 \tag{8}$$

and

$$m^2\beta^2c^2/(1-\beta^2) = (h^2/c^2)\ (\nu_0^2+\nu_\phi^2-2\nu_0\nu_\phi\cos\phi) \tag{9}$$

where β is the ratio of the velocity of the recoiling electron to that of light. It is from these relations that he obtains the formula for the change of frequency

$$\nu_\phi = \nu_0/(1+2\alpha\ \sin^2\tfrac{1}{2}\phi), \text{ where } \alpha = h\nu_0/mc^2 \tag{10}$$

The angle of recoil ψ of the electron may be shown from these equations to be

$$\tan \psi = \frac{\cot \frac{1}{2}\phi}{(1+\alpha)}. \tag{11}$$

Referring again to Fig. 1, it will be assumed that when the impinging corpuscle arrives at B there is a sudden interaction between the corpuscle and the electron, the corpuscle being deflected so as to travel in the direction ϕ. It will be further assumed that the impulse given to the electron will be along the line BO. The problem therefore, is somewhat

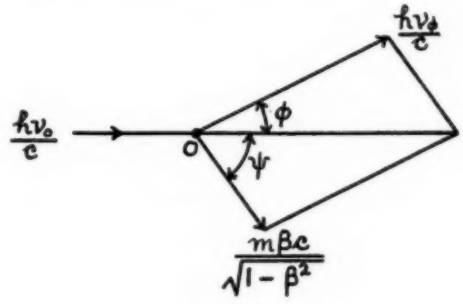

Fig. 2

similar to the oblique impact of two billiard balls of different masses. In the case of the momentum of the corpuscle being small, the angle $\phi = 2\theta$, where θ = angle DOY, OY being perpendicular to the axis of x. The relation between y and θ is therefore given by (6) when 2θ is substituted for ϕ, thus

$$y^2 = (a^2/8)\ (4+3\cos 2\theta+\cos^3 2\theta). \tag{12}$$

In this form the relation holds whether the momentum of the corpuscle is small or large. From Eqs. (1) and (12) we find that the number of corpuscles per cm^2 scattered at an angle ϕ is

$$n_\phi = \frac{3n_0a^2}{8R^2}\ \frac{(1+\cos^2 2\theta)\sin 2\theta}{\sin\phi}\ \frac{d\theta}{d\phi}. \tag{13}$$

This may be expressed in terms of ϕ if we notice from Fig. 1 and Eq. (11) that

$$\tan\theta = \cot\psi = (1+\alpha)\tan\tfrac{1}{2}\phi \tag{14}$$

But the intensity of the x-rays scattered in a direction ϕ by N electrons per unit volume is $I_\phi = N n_\phi h\nu_\phi$. Using the values of ν_ϕ and n_ϕ given by (10) and (13) respectively, this becomes

$$I\phi = \frac{NI_0}{2R^2}\cdot\frac{3a^2}{8}\cdot\frac{(1+\alpha)^2\left\{1+\cos^2\phi+2\alpha(4+6\alpha+4\alpha^2+\alpha^3)\sin^4\frac{1}{2}\phi\right\}}{\left\{1+(2\alpha+\alpha^2)\sin^2\frac{1}{2}\phi\right\}^4\left\{(1+2\alpha\sin^2+\frac{1}{2}\phi\right\}} \tag{15}$$

The radius a can be determined as before by placing the value of I_ϕ when $\phi=0$ equal to the intensity scattered in the forward direction according to Thomson's formula. We thus obtain

$$a=\sqrt{(8/3)}\times(e^2/mc^2)/(1+\alpha) \tag{16}$$

Whence

$$I_\phi=\frac{I_0}{2R^2}\cdot\frac{Ne^4}{m^2c^4}\cdot\frac{\{1+\cos^2\phi+2\alpha(4+6\alpha+4\alpha^2+\alpha^3)\sin^4\tfrac{1}{2}\phi\}}{\{1+(2\alpha+\alpha^2)\sin^2\tfrac{1}{2}\phi\}^4\cdot\{1+2\alpha\sin^2\tfrac{1}{2}\phi\}} \tag{17}$$

The total energy removed from the primary beam due to the scattering process is therefore

$$N\times\pi a^2 I_0=\frac{8\pi}{3}\frac{Ne^4}{m^2c^4}I_0\cdot\frac{1}{(1+\alpha)^2}. \tag{18}$$

Both Eqs. (17) and (18) reduce to Thomson's classical form when $\alpha=0$, i.e., for great wave-lengths.

In Fig. 3, curve I shows for different values of α the total energy removed from the primary beam as expressed by Eq. (18). This energy is divided into two portions, as Compton has pointed out. One part,

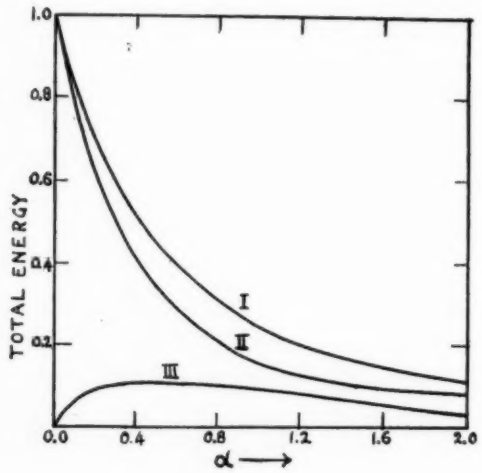

Fig. 3

represented by curve II, reappears as scattered rays, and has been calculated graphically by integrating expression (17) over the surface of a sphere. The second part, shown in curve III, is the energy of recoil of the scattering electrons. It is calculated by taking the difference between curves I and II. In all three curves the unit ordinate is the total energy removed according to the classical theory.

4. Comparison with Experiment

These equations expressing the intensity of the scattered x-rays differ only by second and higher powers of α from the equations derived by A. H. Compton from analogy with the Doppler effect. The differences amount at most to only a few per cent in the region of x-rays, so that in this region the present results are in equally satisfactory agreement with the experiments. For hard γ-rays, however, α is about unity, and in this case appreciable differences arise between these results and those of Compton.

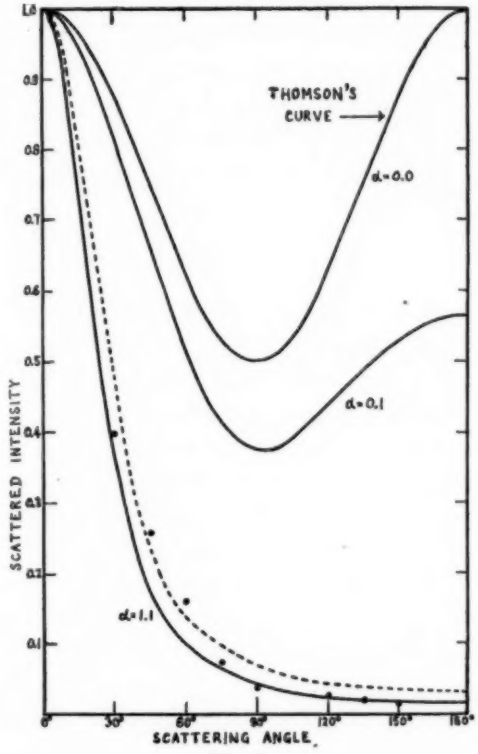

Fig. 4

Ishino's measurement of the total absorption of γ-rays by aluminium and iron[4] and A. H. Compton's measurements of the scattering of hard gamma rays at different angles[5] are perhaps as reliable as any that are available. On the present view, all the absorption of hard γ-rays by the lighter elements is due to the scattering process. Ishino's values of the total mass absorption coefficients for the hard γ-rays from RaC for

[4] M. Ishino, Phil. Mag. **33**, 140 (1917).
[5] A. H. Compton, Phil. Mag. **41**, 758 (1921).

aluminium and iron are 0.066 and 0.063 per gram respectively. According to Eq. (18), taking Compton's estimate of 0.022 A for the wave-length of the γ-rays, these values should be 0.044 for aluminium and 0.043 for iron, whereas Compton's theory gives the corresponding values as 0.061 and 0.059. This agreement is not very satisfactory.

Better agreement is obtained with the scattering experiments on hard γ-rays. Assuming that the ionization measures the intensity of the scattered rays, and taking the unit of scattered intensity as that at $\phi=0°$ according to Thomson's theory, the circles in Fig. 4 are obtained. These points are taken from Compton's paper.[1] Using as before $\lambda=0.022$ A, or $\alpha=1.1$, the lowest solid curve of Fig. 4 is obtained from Eq. (17). The broken curve is plotted from Compton's formula, using the same value of α. The experimental points fall somewhat more closely on my curve than on Compton's. Taking these tests as a whole, we must conclude that the accuracy of the experiments is not sufficient to decide which formula is the more nearly accurate.

5. Discussion

It has been shown that a corpuscular quantum theory which will give scattering according to Thomson's theory when long wave-length x-rays are used will also give a formula representing very well the experimental values of the scattering when short wave-length x-rays are used. Such differences as do occur may be explained as being due either to experimental error or to some unwarranted approximation in the theory. In the derivation of formula (17) it should be remembered that the value of the scattering at $\phi=0°$ has been assumed equal to that given by Thomson's theory at $\phi=0°$. The effect of this has been to cause the "radius" a of the electron to be a function of α and therefore of the wave-length. Also, the corpuscles have been considered as mathematical points. The "radius" may be the "radius" of the electron plus the "radius" of cross section of the quantum. Further, referring to Fig. 1, it has been assumed that for the same value of y/a, the angle BOY or θ remains the same no matter what the wave-length of the incident quantum may be, even though a changes with the wave-length. That is, although the "size" of the electron changes, yet the "shape" as represented by the relation between y/a and θ in (12) remains the same. If the "shape" varies with α, then expression (12) no longer holds.

Let us introduce a new variable A defined by the relation

$$\tan A=[\sqrt{(1+F)}/(1+\alpha)]\tan\theta=\sqrt{(1+F)}\tan\tfrac{1}{2}\phi \qquad (19)$$

where F is any function of α which becomes zero when $\alpha=0$. In order

to bring about distortion of the "shape" of the electron, we shall replace θ by A in (12) and we obtain

$$y^2=(a^2/8)\,(4+3\cos 2A+\cos^3 2A). \tag{20}$$

This leads then to

$$I_\phi=\frac{I_0}{2R^2}\cdot\frac{Ne^4}{m^2c^4}\cdot\frac{\{1+\cos^2\phi+4F(1+\frac{1}{2}F)\sin^4\frac{1}{2}\phi\}}{\{1+F\sin^2\frac{1}{2}\phi\}^4\cdot\{1+2a\sin^2\frac{1}{2}\phi\}} \tag{21}$$

which takes the place of (17), and

$$N\pi a^2 I_0=\frac{1}{(1+F)}\cdot\frac{8\pi}{3}\cdot\frac{Ne^4}{m^2c^4}\cdot I_0 \tag{22}$$

which replaces (18). Putting $F=2a$, Compton's formulas for I_ϕ and the scattering absorption coefficient are obtained from Eqs. (21) and (22) respectively. Putting $F=2a+a^2$, my formulas (17) and (18) are obtained. Hence, while the corpuscular theory gives the results stated in the earlier parts of this paper if no distortion of the electron is assumed, by postulating the appropriate distortion Compton's formula or any approximately similar formula may be derived.

In spite of these somewhat uncertain assumptions, formulas have, however, been derived from the corpuscular hypothesis which agree well with experiment. If a law of force between the quantum and the electron could be found such as to give Thomson's scattering formula for small values of h/λ, then possibly the true form of F in (21) could be attained.

It is perhaps worth noticing that the quantity a in these formulas is equal to the ratio of the equivalent mass of the quantum to the rest-mass of the electron.

In conclusion, the writer wishes to thank Professor A. H. Compton for much interesting discussion in regard to the subject of this paper.

WASHINGTON UNIVERSITY,
ST. LOUIS, MO.,
February 24, 1923.

THE SCATTERING OF LOW SPEED ELECTRONS BY PLATINUM AND MAGNESIUM

By C. Davisson and C. H. Kunsman

Abstract

Scattering of electrons by platinum and magnesium.—Electrons from a tungsten filament were accelerated with voltages up to 1000, and a restricted beam was directed against a platinum target at 45° incidence. The number of scattered electrons with over 9/10 the energy of the primaries was determined for various directions by measuring the current to a Faraday box collector which could be revolved so as to explore the range from within 15° of the primary beam ($\Psi = 15°$) to the plane of the target ($\Psi = 135°$). For bombarding potentials up to 200 volts the intensity of scattering decreases more or less regularly from low to high values of Ψ, indicating a maximum for $\Psi = 0$. At higher potentials the scattering pattern develops two well marked lobes besides the one for $\Psi = 0$. When the platinum target was covered with a deposit of magnesium the patterns found are simple with the exception of a small lobe on the curves for potentials less than 150 volts. Up to 500 volts the maximum intensity is apparently in the direction $\Psi = 0$, but for higher voltages the direction shifts to around $\Psi = 90°$. *Theoretical interpretation.* Since low speed electrons are more easily deflected than α-particles, their scattering patterns depend not only on the field immediately about the nucleus but also upon its nature in regions beyond various or all of the structural electrons. The complicated patterns for platinum are taken to indicate that the field out from the nucleus in the platinum atom is characterized by several approximate discontinuities resulting from more or less definite concentrations (shells) of electrons at certain distances from the center. The magnesium atom having a single strong concentration of electrons (the L group) gives rise to simple patterns.

Arrangement of electrons in the magnesium atom.—The simple patterns for Mg agree in the main features with theoretical patterns calculated for the scattering of electrons by a positive nucleus of limited field (Davisson, Phys. Rev. **21**, 637, 1923). On the basis of this theory the results indicate a concentration of 7 or 8 electrons in a shell with a radius of about 1.5×10^{-9} cm. The theory has not been sufficiently developed to permit an analysis of the patterns for Pt.

I. Introduction

WHEN a stream of electrons is directed against a metal target the area under bombardment becomes temporarily a source of electron emission. The results of numerous investigations[1-12] have established that a part at least of this emission is made up of electrons, originally in the target, that have been expelled in some way by the incident or primary electrons. This is certain from the fact that ordinarily there can be found a range of bombarding potentials over which the number of electrons pro-

ceeding from the target exceeds the number incident upon it. Whether or not the whole of the emission is made up of such secondary electrons is a question that in the nature of the case has been less definitely answered. Baeyer,[1] Gehrts[2] and Campbell[3] observed that for bombarding potentials up to about 12 volts the emission is comprised in part of electrons whose speeds are not appreciably less than that of the primaries, and inferred that these were primary electrons that had been turned back from the target. At higher potentials, however, this class of electrons was not detected. As the bombarding potential was increased beyond 12 volts the maximum speed of the emitted electrons was found to fall below that of the primaries and finally to reach a limiting value which was independent of further increase in the speed of the incident particles. In observations extending to 3000 volts this particular result has been obtained repeatedly. The limiting speed has been fixed by different observers as corresponding to potential differences of from 5 volts to 40 volts. Quite recently, however, experiments have been described by Farnsworth[12] in which electrons of all speeds up to that of the primaries were observed proceeding from a nickel target for bombarding potentials up to 110 volts. Results similar to those of Farnsworth were also obtained several years ago in this laboratory by W. Wilson and J. R. Weeks for a number of metals and for bombarding potentials up to 250 volts. Unfortunately the results of these measurements have not been published.

Experiments are described in this paper from which it is evident that electrons having speeds not appreciably less than that of the primaries proceed from platinum and magnesium for all bombarding potentials up to the highest investigated in each case, 1000 volts and 1500 volts, respectively. In preliminary notes[13] we have also described similar results obtained in experiments with targets of nickel and aluminium.

These relative high speed electrons make up only a small fraction of the total number leaving the target, particularly at high bombarding

[1] Baeyer, Verh. Deut. Phys. Ges. 96 and 953, 1908; Phys. Zeit. **10**, 176, 1909
[2] Gehrts, Ann. der Phys. **36**, 995, 1911
[3] Campbell, Phil. Mag. **25**, 803, 1913; **28**, 286, 1914; **29**, 369, 1915
[4] Horton and Davies, Proc. Roy. Soc. A **95**, 408, 1919
[5] Hull, Phys. Rev. **7**, 1, 1916
[6] Dadourian, Phys. Rev. **14**, 434, 1919
[7] Millikan, Proc. Nat. Acad. Sci. **7**, 13, 1921
[8] Barber, Phys. Rev. **17**, 323, 1921
[9] Tate, Phys. Rev. **17**, 395, 1921
[10] McAllister, Phys. Rev. **19**, 247, 1922
[11] Baltruschat and Starke, Phys. Zeit. **23**, 403, 1922
[12] Farnsworth, Phys. Rev. **20**, 358, 1922
[13] Davisson and Kunsman, Science, **64**, 522, Nov. 25, 1921; Phys. Rev. **19**, 253 and 534, 1922.

potentials. In a tube exhausted to 10^{-7} mm of mercury they can be observed without difficulty, but at higher pressures their detection becomes uncertain or impossible on account of the masking effect of positive ions. It can hardly be regarded as surprising, therefore, that they have avoided detection rather consistently, particularly as much of the experimenting in this field was done prior to the development of present day vacuum technique.

II. Theoretical Considerations

The view taken in this paper in regard to these electrons that proceed from the target with very nearly the speed of the primaries is that they are themselves primary electrons that have been scattered without appreciable loss of energy in encounters with single atoms in or near the surface of the target. The mechanism is assumed to be similar to that of α-ray scattering but to differ from it in certain respects. An α-ray, on account of its large ratio of kinetic energy to charge, is unappreciably deflected except at distances from a nucleus that are less, in general, than the distance to the nearest structural electrons. The angle distribution of the scattered particles is dependent only upon the nature of the field at these small distances. A low speed electron, however, is much more easily deflected. It may pass quite outside various of the groups of structural electrons and still be turned through a large angle. It is to be expected, therefore, that the angle distribution of these particles will depend upon the arrangement of electrons in the atom as well as upon the nature of the field near the nucleus. If the electrons are arranged in a number of more or less definite shells the scattering pattern will exhibit irregularities determined by the constants of these shells and the speed of the bombarding electrons. If the electrons are arranged in a single strong shell correspondingly simple patterns are to be expected.

A calculation has been given recently by one of us[14] of the angle distribution of electrons scattered by a positive nucleus whose field ends abruptly at a distance ρ from the center. It was shown that the intensity of scattering in a direction making an angle Ψ with the primary beam will be given by

$$I_\Psi = \text{const}\left(\frac{2\mu-1}{(2\mu-1)^2\ (1+\cos\Psi)+(1-\cos\Psi)}\right)^2$$

where $\mu = V\rho/E$. V is the potential drop through which the incident electrons acquire their speed, and E the nuclear charge.

[14] Davisson, Phys. Rev. **21**, 637, 1923

One object of this investigation has been to find if this formula is at all capable of representing the scattering patterns of magnesium (atomic number 12). The magnesium surface was formed by sublimation on a target of platinum, so that it has been possible by making observation before and after forming the deposit to determine the patterns for both metals.

III. The Experimental Method

The experimental tube is shown diagrammatically in Fig. 1. The principal parts are the tungsten filament F_1, for supplying electrons, the nickel cylinder and chute C, for limiting the cross-section of the bombarding stream, the platinum target T and the double Faraday box collector B_1 and B_2. The target system, comprising the target proper, a

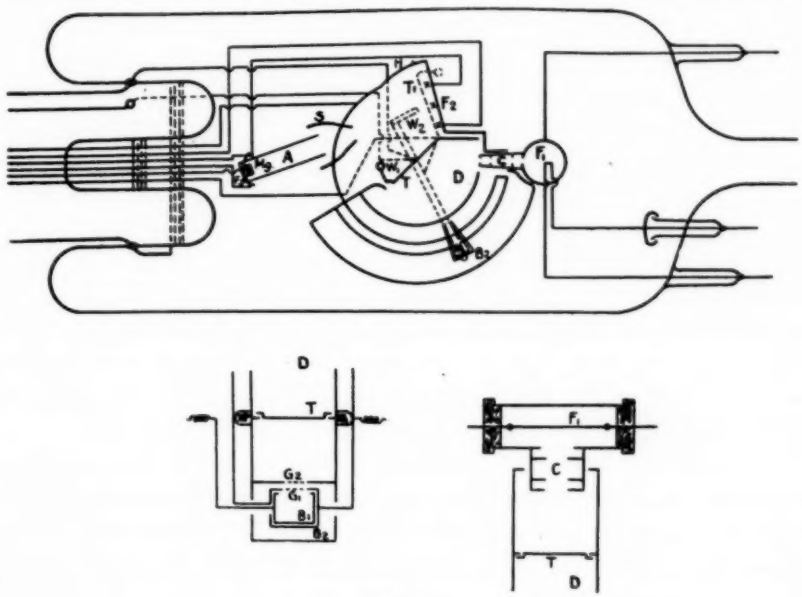

Fig. 1.

counterpoise W_1 and a shielding plate which is shown making an angle with the target, is arranged to rotate about an axis coincident with the junction of the target and shielding plate. By tilting the tube the target can be made to take either of two extreme positions. The normal position is that indicated in section by solid lines and designated as T. The second position is that indicated in section by dotted lines and designated as T_1. In this position the target is brought in range of a tungsten filament F_2, from which it can be heated by electron bombardment for the purpose of cleaning its surface. In this position the target is also in range

of the "magnesium gun" shown at A. This gun is a platinum cylinder, closed at one end and charged with a small piece of magnesium held in place in the closed end of the tube. A tungsten filament F_3 serves as source of electrons for heating the cylinders by bombardment, and a glass shield S protects various parts of the apparatus from magnesium vapor. The shielding plate which has already been referred to as a part of the target system also serves this purpose.

The filament F_1 is located accurately in the axis of the nickel cylinder, and is held taut by a molybdenum spring not shown in the diagram. A series of apertures in the cylinder and chute for limiting the stream of bombarding electrons from the filament, is clearly indicated in the figure. The three apertures in the chute are each 6 by 1.5 mm, and that in the cylinder is somewhat larger. From the filament to the furthest aperture is a distance of 19 mm, and this also is the distance from this aperture to the center of the target.

The target in its normal position forms with the chute and other metal parts a complete enclosure. These other metal parts suggest a section of a drum and will be referred to collectively as the drum. The axis is parallel to F_1 and passes through the center point of the target face. In making measurements the cylinder and chute, the target, and the drum, which are insulated from one another, are ordinarily held at the same potential positive to F_1. The bombarding electrons thus acquire their speed within the cylinder, and proceed through the apertures to the target, on which they are incident at 45°, without further acceleration. It will be seen from the geometry of the system that the area under bombardment is approximately 6 mm (parallel to F_1) by 4 mm.

The double Faraday box collector is swung on a pair of arms pivoted in the axis of the drum so that the collector revolves in an arc of a circle about the source of the scattered electrons. Two cylindrical flanges fixed to the inside of the drum are interposed between the target and the collector as shown at G_2 in one of the detail drawings. The opening between their inner edges (6 mm wide) is covered by a grid formed of two sets of fine wires stretched diagonally across the opening at right angles to each other.

The opening in the outer Faraday box is 6 by 1.5 mm and is covered by grid wires. The opening in the inner box is somewhat larger and is not so covered. The two parts of the box are insulated from one another by thin quartz plates. The lead from the inner box is especially protected from stray electrons that might reach it inside the tube. From its point of emergency from the outer box to the point at which it passes through the wall of the tube it is completely encased in small quartz tubing.

The various parts of the apparatus are supported from three glass rods fixed in the base of the tube. These are not shown in the figure. The numerous leads are brought out through the base of the tube and through ears in the top. Those to the target, drum and collector are separated as far as possible from the others and guard rings are interposed to protect them from leakage currents.

All metal parts were thoroughly pre-glowed in a vacuum oven immediately before assembly. During baking and pumping such of the parts as could be bombarded by electrons were raised to high temperatures for considerable periods. The complete unit sealed to the pumps comprised, besides the experimental tube, an ionization manometer and a narrow side tube containing cocoanut charcoal, which was held at 460° C throughout the pumping period. The unit was sealed from the pumps with the pressure at about 10^{-5} mm of mercury and with the charcoal tube at 450° C. On cooling the charcoal with liquid air the pressure became less than could be measured, i.e. less than 10^{-8} mm of mercury. Liquid air was maintained on the charcoal during the entire period of the measurements.

The tube was mounted with the axis of the drum parallel to the horizontal component of the earth's magnetic field. The angular position of the collector could then be varied by rotating the whole tube about this axis, the collector system hanging as a pendulum. The angular range thus covered was from within 15° of the primary beam to somewhat beyond the plane of the target. The earth's magnetic field could be compensated, when this was desirable, by means of appropriate Helmholtz coils.

IV. Experimental Results

Platinum. In making observations we have ordinarily worked with what we have termed "ten per cent" electrons, that is, electrons that leave the target with losses in energy that do not exceed ten per cent of their incident energy. If, for example, the distribution of this class of electrons was to be determined for a bombarding potential of 100 volts, the cylinder and chute, the target, and the drum were held at +100 volts relative to the mid-point of the filament, and both boxes of the Faraday collector at +10 volts. There was thus a retarding potential of 90 volts between G_1 and G_2 (Fig. 1), and only electrons that had left the target with 90 volts energy could enter the collector. With this arrangement of potentials the currents to the drum, target, and collector were measured, and the ratio of the collector current I_c to the total current received by drum and target I_t, was evaluated as a measure of the

intensity of scattering for the particular angular setting of the collector. The sum of the currents to the target and drum measures, to a close approximation, the total number of electrons incident per second on the target, and I_c measures the corresponding number entering the inner box. The total current I_t ranged from 3×10^{-6} to 9×10^{-5} amperes, and was measured with an ordinary wall type galvanometer. The current I_c varied in different measurements from 10^{-5} to 10^{-3} of the total current and was measured with a Leeds and Northrup galvanometer of high sensitivity, 1.5 $(10)^{-10}$ amp. per mm deflection.

Four sets of distribution curves for platinum are shown in Fig. 2, covering the range of bombarding potentials from 10 to 1000 volts.

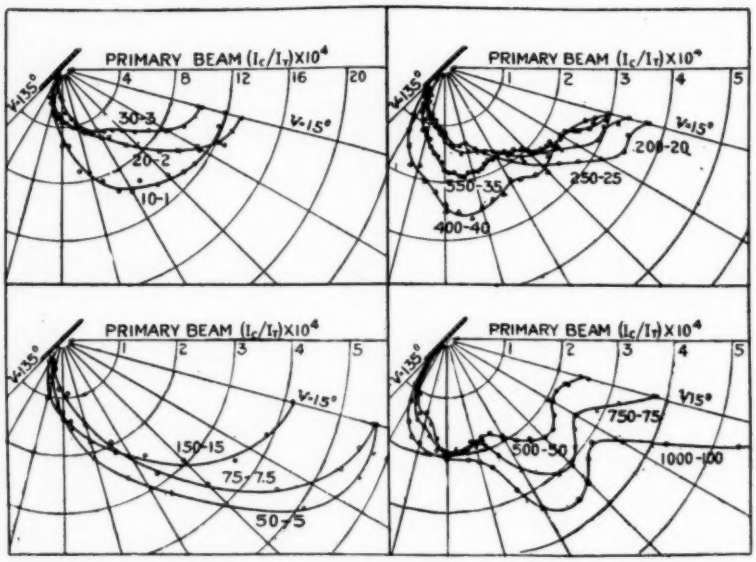

Fig. 2. Angular distribution of electrons scattered by platinum.

The notation "30-3" is used to indicate that the bombarding potential was 30 volts and the collector potential 3 volts. All curves in this figure are for "ten per cent electrons." It will be noted that for bombarding potentials up to 200 volts the distribution of the scattered electrons is comparatively simple, much more simple than might reasonably be expected for the scattering by an atom as complex as that of platinum. Above 200 volts, however, the expected irregularities are much in evidence. The development of various lobes and their variation in angular positions with increase in bombarding potential can be easily traced. All of these curves are quite reproducible and are independent of the total bombarding current over a wide range.

In Fig. 3 additional curves are shown for bombarding potentials 500 and 1000 volts. The three curves for 500 volts corresponding to three different values of the retarding potential. With the collector at 10 volts, the electrons entering the collector left the target with at least 98 per cent of their incident energy, or 99 per cent of their incident speed. The 1000 volt curves are likewise for a series of three different collector potentials as indicated in the figure. It will be noted that the measured intensity of the scattering in a given direction is about proportional to the collector potential. This is at least an indication that the two vanish together, and that, therefore, some among the scattered electrons have speeds not appreciably less than that of the primaries. As the collector potential is decreased the various features of the pattern stand out more sharply; otherwise the form of the curve is independent of the retarding potential over the range explored.

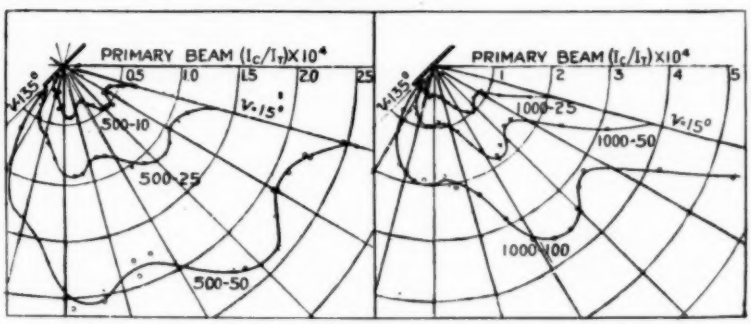

Fig. 3. Angular distribution of electrons scattered by platinum.

The means of analyzing distribution curves in terms of the present theory are not sufficiently developed to permit of a quantitative consideration of patterns as complex as these exhibited by platinum. The most that can be said at present is that they indicate several distinct concentrations of electrons in the platinum atom at various distances from its center.

Magnesium. A light deposit of magnesium was formed on the platinum target by the method already described, and a series of distribution curves obtained for bombarding potentials to 1500 volts. No means were available for estimating the thickness of this deposit. The vaporization was continued very gently until a barely visible spot had been formed. A second deposit was then formed on top of the first, and the series of observations repeated.

A set of these curves for bombarding potentials from 24 to 1500 volts is shown in Fig. 4. With the exception of a small lobe or spur which is noticeable near $\Psi=90°$ on curves in the range 24 to 125 volts, the dis-

tributions are strikingly simple and conform in a general way to the requirements of the theory for the scattering by single shell atoms. Starting from $V=24$ volts the elongation of the pattern in the direction $\Psi=0$ first increases with V, and then decreases, the intensity in the direction $\Psi=0°$ finally becoming less than in the direction $\Psi=90°$. This behavior is sufficiently like that calculated for the idealized system to warrant our neglecting the small spur for the present and attempting a calculation of the radius of the shell from the characteristics of the principal feature of the patterns.

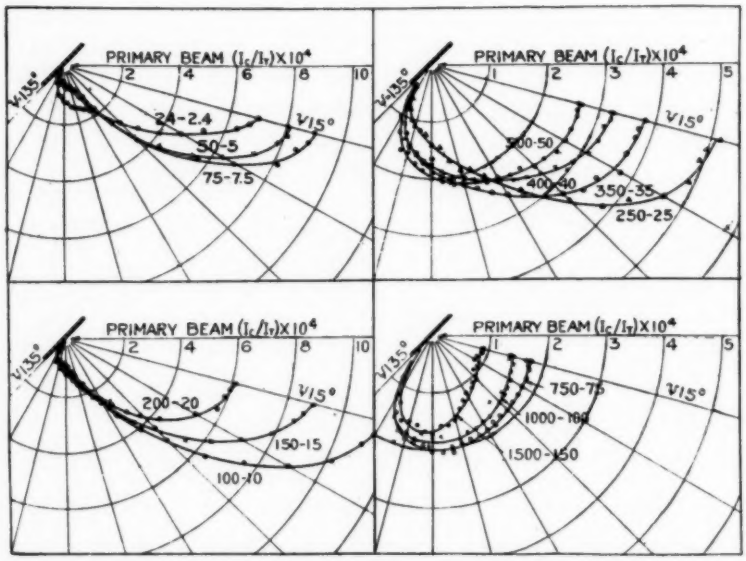

Fig. 4. Angular distribution of electrons scattered by magnesium.

It is important to recognize, in dealing with the curves quantitatively, that the form of each is determined in part by the absorption of scattered electrons in the metal. Experiments with a tube in which the target can be rotated, indicate that many of the scattered electrons receive their large deflections at considerable depths in the metal and are subjected to absorption on their way to the surface. The effect of this absorption is to reduce the observed intensities differently in different directions, least in the direction normal to the surface and most in the directions in its plane. In the plane of the target the observed intensity is always zero. This results from absorption and partly perhaps from the microscopic roughness of the surface.

The form of the observed curves must also be affected to some extent by the variation in angular width of the bombarded area as viewed from the collector. This width is greatest when the collector stands in the

normal to the target, and in this position fewer electrons enter the collector than would if the bombardment were more concentrated. As the collector moves out of this position the bombarded area is viewed more nearly edge on, and the apparent intensities are somewhat increased. Fortunately, the effects both of the absorption and of the variability of angular width of the source should be symmetrical with respect to the normal to the target. We may reasonably expect, therefore, that the ratio of observed intensities in directions making equal angles on opposite sides with the normal will be the same as if the distribution curves were ideal.

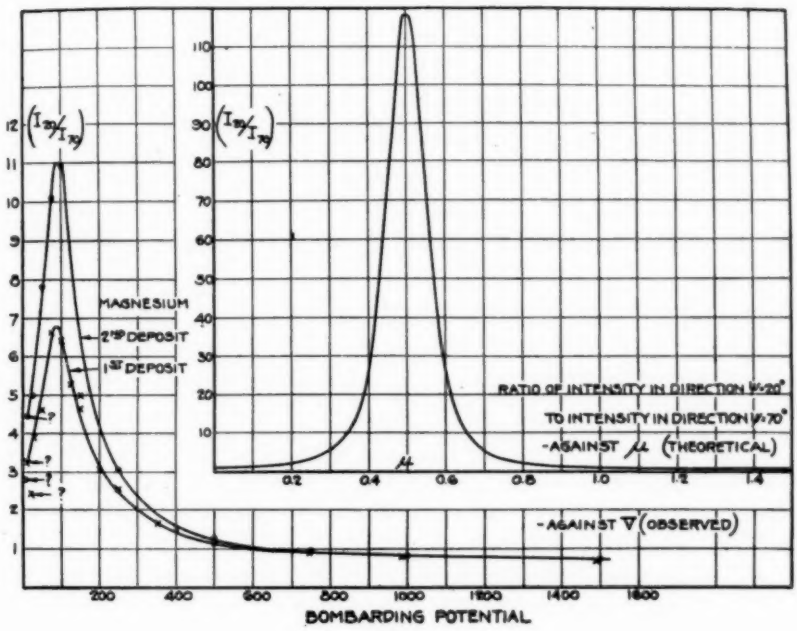

Fig. 5.

In Fig. 5 we have plotted the ratios of observed intensities for directions $\Psi = 20°$, $(45-25)$, and $\Psi = 70°$, $(45+25)$, against bombarding potentials. It should be mentioned that in the distribution curve for 24 volts the lobe is a definite feature extending to a value of Ψ less than 70°. In this case the ratio of intensities plotted in Fig. 5 is that between the actual intensity at 20° and the intensity at 70° as read from an extrapolation of the main distribution. At potentials less than 20 volts the main distribution and the lobe are apparently merged and indistinguishable. The ratios for these voltages have been taken directly from the distribution patterns and plotted in Fig. 5. They have been disregarded, however,

in drawing in the curves in this figure. We have no explanation for the fact that the maximum of the curve for the second deposit is higher than that for the first.

V. Comparison with Theory

The relation to be expected between this ratio and μ (proportional to V) can, of course, be calculated from the formula for I_ψ. It is shown graphically in the same figure to one tenth the vertical scale of the observed curves. The outstanding differences between the theoretical and the observed curves are (1) the difference in height of their maxima, and (2) the difference in position of their maxima relative to other features of the curve. It seems not unlikely that the former of these differences results merely from the fact that the field about the nucleus is not as sharply limited as assumed in arriving at the theoretical curve. The position of the observed maximum at 90 volts instead of much further to the right has the appearance of being a more serious discrepancy. It is significant, however, that each experimental curve, so far as it has equal ordinates on the two sides of its maximum, is reasonably symmetrical. The experimental curve can be most simply described as one resembling the theoretical curve in form that has been shifted several hundred volts to the left. That is, the scattering is reasonably in accord with what might be expected if the bombarding potential were in each case several hundred volts greater than that actually used. This suggests that the nucleus is surrounded by a shell of electrons which does not completely compensate its charge, and that the several hundred additional volts are acquired by the incident electrons in the field external to this shell. The incident electrons would, of course, be deflected to some extent in such a field. The principal effect, however, should be to increase their velocity toward the limited field. This is particularly true as we are dealing only with those electrons that suffer large total deflections, that is, with those that pass nearest the nucleus, and, therefore, approach most nearly head-on. For the present we shall assume that this is the cause of the shift, and disregard the deflections that are involved.

Next to the position of the maximum at $V=90$ volts, the most dependable result from the experimental curve would appear to be the potential at which the ratio of intensities falls to unity. This occurs at $V=650$ volts. Approximately the same value of this potential is obtained when curves are plotted for other pairs of values of Ψ satisfying the condition $\Psi_1+\Psi_2=90°$. $650-90=560$ volts should then correspond to the value of V in the equation $\mu=\frac{1}{2}=V\rho/E$, which leads to

$$E/\rho=2\times560/300=3.73 \text{ e.s.u./cm}$$

where E is the central charge and ρ is the radius of the shell.

On this basis the amount of the voltage shift is $560-90=470$ volts. Using E' to represent the residual charge of the atom out to and including the principal shell of electrons, and regarding the field outside this shell as essentially unlimited, we also have

$$E'/\rho=470/300=1.57 \text{ e.s.u./cm.}$$

Combining these results, $E'/E=0.42$. This is the ratio of 5 to 12, so that, if the central charge is $12e$, the residual charge of nucleus and shell should be $5e$, indicating a shell of seven electrons with the remaining five considerably outside this shell. On the other hand if two K-electrons are assumed so near the nucleus that the central charge is effectually $10e$, then the ratio of E' to E would indicate six electrons in the L-shell and four others outside these, while the assumption of three K-electrons would lead to the arrangement three-five-four. If the central charge is $12e$ then

$$\rho=(12\times 4.78/3.73)\ (10)^{-10}=1.54\times 10^{-9} \text{ cm.}$$

For central charges $10e$ and $9e$ the values of ρ are respectively $1.28\ (10)^{-9}$ cm and $1.15\ (10)^{-9}$ cm. These values are smaller but reasonably in accord with the radius of the two quantum circular orbit of the magnesium atom as calculated on Bohr's theory. If the radius of the one quantum orbit of the hydrogen atom is $a_0=5.3\times 10^{-9}$ cm, then for nuclear defect zero the radius of the two quantum orbit in the magnesium atom should be $a=4a_0/12=1.8\times 10^{-9}$ cm. For nuclear defect $3e$ we would have $a=4a_0/(12-3)=2.6\times 10^{-9}$ cm.

We return now to the small lobe which is a feature of the distribution curves for bombarding potentials up to 125 volts. It is conceivable that this lobe is due to electrons which have been deflected only in the field outside the principal shell. For such a class of electrons the principal shell would function as an obstacle. Only those electrons would appear in the distribution whose trajectories lay entirely outside its boundary. If the external field due to the residual charge E' be regarded as essentially unlimited, we have, from the ordinary theory of conic orbits, that the nearest approach of an electron to the center of the system

$$b=\frac{E'}{2V}\left[\left(\frac{2}{1+\cos\Psi}\right)^{\frac{1}{2}}-1\right].$$

The distribution we are considering would then include only electrons for which b is as great or greater than ρ. It would begin abruptly at the critical value of Ψ which satisfies the above equation with b set equal to ρ, and would be altogether lacking in the angular range below this value. It will be seen that this critical value of Ψ should increase with increase in V. In Fig. 6 we have reproduced the portions of distribution curves for bombarding potentials up to 125 volts which include the small lobe.

The radial scales of these curves are arbitrary and have been adjusted to avoid overlapping. It will be seen that the value of Ψ at which the added distribution begins is fairly definite, and that it does, in fact, increase with increase in V.

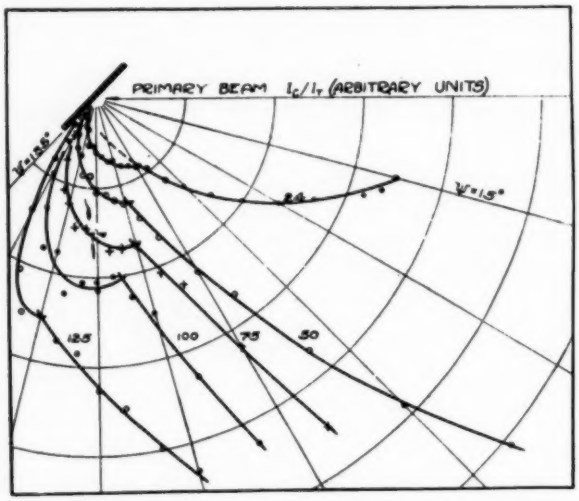

Fig. 6. Portions of distribution curves of magnesium showing lobe.

Setting b equal to ρ and rewriting the equation in the form

$$\left[\left(\frac{2}{1+\cos\Psi}\right)^{\frac{1}{2}}-1\right]=\frac{2\rho}{E'}V$$

we see that the function of the critical value of Ψ on the left should be proportional to V, the factor of proportionality being $2\rho/E'$. The values of this function for all of the curves in which Ψ can be located are plotted against V in Fig. 7. The line through the origin has been drawn in without reference to the plotted points. Its slope is $2\rho/E'$ as computed from the value of E'/ρ found in the calculation based on the main feature of the patterns. The observed points fall on this line as well perhaps as might be expected.

This explanation of the lobe would be untenable, of course, if it should turn out that the lines along which the electrons must be assumed to approach are as distant from the scattering center as the distance between adjacent atoms in the magnesium crystal. That this is not the case is clear from the following considerations. If d represents the distance from the center of force to the line along which an electron approaches, ρ the distance from the force center to the apse of its orbit, and Ψ the direction in which the electron finally proceeds from the system, it can be shown

that in the case of an unlimited field these quantities are related through the equation

$$d=\rho\left[\frac{(1-\cos\Psi)^{\frac{1}{2}}}{\sqrt{2}-(1+\cos\Psi)^{\frac{1}{2}}}\right].$$

The largest values of d correspond to the smallest values of Ψ. The minimum observed value of the critical angle in any of the curves is 55°. For this case $d=4.1\rho$. Or, if we use 1.5×10^{-9} cm as the value of ρ, $d=6.1\times10^{-9}$ cm. The electrons forming the added distribution in this extreme case would then approach along lines not less than 6×10^{-9} cm

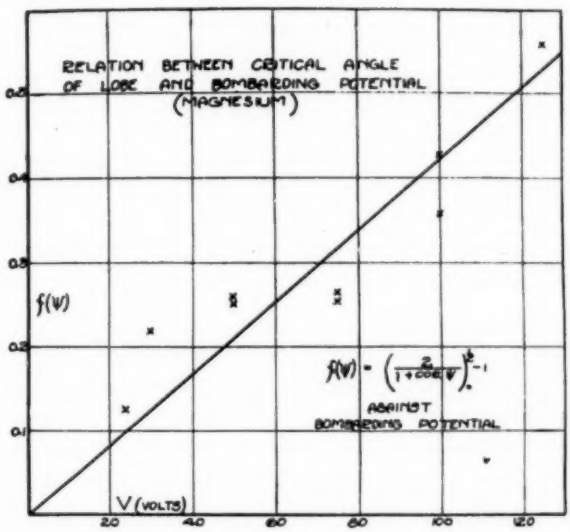

Fig. 7.

from the center of the atom. This distance is about one-fifth the shortest distance between atoms in the magnesium crystal. It appears, therefore, that it would be possible under favorable circumstances for electrons to have approximately ideal encounters of the sort considered with single atoms, even in the extreme case corresponding to $\Psi=55°$.

We now inquire within what distances, on the present theory, the scattered electrons forming the main distribution have approached to the center of the system. It may be shown in the case of the limited field that if the distance of nearest approach b is expressed as a fraction a of the radius of the field ($b=a\rho$), then a will be related to the other quantities involved through the equation

$$a=\delta^2\left[\frac{2\mu}{1+[1+4\mu(\mu-1)\delta^2]^{\frac{1}{2}}}\right]$$

where

$$\delta = \left(\frac{d}{\rho}\right)^2 = \left[\frac{(1-\cos\Psi)}{(1-\cos\Psi)+(2\mu-1)^2\,(1+\cos\Psi)}\right]$$

d being the distance from the nucleus to the line of approach. A table of values of α calculated from this equation and applicable to the present results is given below.

TABLE I

μ	V (Volts)	α ($\Psi=15°$)	α ($\Psi=45°$)	α ($\Psi=90°$)
0.45	34	0.35	0.68	.78
0.50	90	1.00	1.00	1.00
0.55	146	0.43	0.83	0.95
0.75	370	0.049	0.33	0.73
1.00	650	0.017	0.15	0.50
1.50	1210	0.0065	0.060	0.26
2.00	1770	0.0038	0.037	0.17

Of the electrons forming the observed patterns those scattered in the direction $\Psi=15°$ when V had its maximum value (1500 volts) passed nearest the nucleus. For these $\alpha=.005$. If $\rho=1.5\times10^{-9}$ cm then the nearest approach was 7×10^{-12} cm. This is about double the distance of nearest approach estimated in the experiments on alpha ray scattering. The distance is much less, however, than the radius of the orbit of the K electrons as calculated on Bohr's theory. If $a_0=5.3\times10^{-9}$ cm then the K-electrons in the magnesium atom should be at a distance from the nucleus given approximately by $a_0/(12-\frac{1}{4})=0.45\times10^{-9}$ cm. This distance corresponds to $\alpha=\frac{1}{3}$. It is clear then from the figures in Table I that over a wide range of V certain electrons pass tangent to a sphere of this radius and emerge in the angular range $\Psi=15°$ to $\Psi=90°$. In Table II we have written down the angles corresponding to $\alpha=0.33$ for values of V for which curves are shown in Fig. 4.

TABLE II

V:	24	50	75	(90)	100	150	200	250	500	750	1000
μ:	0.44	0.46	0.485	(0.5)	0.51	.55	0.60	0.64	0.87	1.09	1.31
Ψ:	15°	10°	3°	(0°)	3°	12°	21°	28°	59°	78°	90°

If there are irregularities in the distribution curves caused by the K-electrons at or near these angles they are too slight to be detected with the present experimental arrangement. In particular it seems impossible to associate the small lobe at low voltage in any way with the K-electrons.

We must conclude then that on the basis of the present interpretation and within the accuracy of the measurements there is no evidence of

any orbital electrons in the range 7×10^{-12} cm to 1.5×10^{-9} cm from the nucleus. The spherical shell system of central change $12e$ that would yield patterns most nearly in accord with those observed is one in which the central charge is surrounded by a single shell of charge $-7e$ and of radius 1.5×10^{-9} cm.

VI. Discussion of Results

In attempting to infer the nature of a scattering system from the angular distribution of scattered particles the only possible method of procedure seems to be to calculate distribution patterns for systems of assumed characteristics and to compare these with the observed distribution. If the calculated distribution can be made to represent the experimental results by an appropriate choice of constants the assumed system is similar to the actual system, at least in the way it scatters particles. It is not necessarily similar to it in other respects, nor does it follow that other models might not be found that would also be similar to the actual system in this particular respect. This limitation to the use that can be made of the data of scattering experiments has been stated very clearly by C. G. Darwin.[15]

In the present case we have compared the observed distribution curves with those calculated for an assumed system which is admittedly inadequate to represent any actual atom, except in the most hazy manner. Recognizing this deficiency in the model it has seemed legitimate to see in any agreement between the two sets of curves, however general, an equally general agreement between the atomic system and the model. It has also seemed legitimate to take advantage of this general agreement to calculate the constants of the model. It should be recognized, however, that the constants are primarily those of the model and not those of the atom. In the present case the constants are those of the spherical shell model that most nearly resembles the actual system in the way that it scatters electrons. These are not necessarily related in any very simple way to the constants of the actual system. It has not been shown, for example, that the spherical shell that most nearly represents a cubical arrangement of eight electrons when appropriately integrated over all orientations is a shell of charge $8e$ and of radius equal to the distance from the center to a corner of the cube. The octet might very well be most nearly equivalent to a more contracted shell of fewer than eight charges plus a certain external field. If the electrons are arranged as in the Bohr model with half of the L-electrons moving in elliptical orbits it is difficult

[15] Darwin, Phil. Mag. **12**, 486, 1921.

to conjecture the probable relation between the actual system and its most nearly equivalent spherical shell model. This is particularly true as the system not only has directional properties, but in a particular orientation also presents a variety of aspects to incident electrons depending upon the phases of the structural electrons in their orbits. At all except the lowest bombarding potentials the time of transit of the electron through the atom is small compared with the periods of the orbital electrons.

No attempt has been made to give a separate interpretation of the results in terms of the scattering patterns which are found when it is assumed that the electrons in passing through the atom execute orbits of the type calculated by Darwin. So far as we can judge from a careful examination of the curves there is no evidence that the electrons have executed these orbits. On the simple theory, or on H. A. Wilson's view in regard to encounters between an electron and a positive nucleus,[16] identical patterns are to be expected for bombarding potentials V_1 and V_2 satisfying the condition $V_1+V_2=2V_m$, where V_m is the potential for which the pattern has its maximum elongation. On the basis of Darwin's orbits, however, these curves would be expected to exhibit differences in form of the type shown in Fig. 7 of the theoretical article.[14] A comparison of the magnesium curves for potentials 24 and 150 volts, and for 50 and 125 volts shows that the curves of each of these pairs have closely the same form. It should be pointed out, however, that the differences in form to be expected between the curves of these pairs on the basis of Darwin's calculations is much less than shown in the figure referred to. The curves in the figure are for $\mu=\frac{1}{4}$ and $\mu=\frac{3}{4}$, while the values of μ for the curves which have been compared are, as we suppose, much closer to the value one-half. In any event the calculations which have been based on the critical voltages read from the curve in Fig. 5 would not be appreciably affected by assuming that the electrons had executed Darwin orbits.

In conclusion we take pleasure in expressing our thanks to Dr. H. D. Arnold and Dr. W. Wilson for encouragement to carry out this investigation and to G. E. Reitter for the care with which he constructed the special apparatus required.

RESEARCH LABORATORIES OF THE
AMERICAN TELEPHONE AND TELEGRAPH COMPANY
AND THE WESTERN ELECTRIC COMPANY, INCORPORATED,
April 11, 1923.

[16] Wilson, Proc. Roy. Soc. A **102**, 9, Oct. 2, 1922.

AN EQUILIBRIUM THEORY OF ELECTRICAL CONDUCTION

By A. T. Waterman

Abstract

Equilibrium electron theory of electrical conduction.—(1) *General equation.* Accepting the simple electron theory expression for specific conductivity, the concentration of free electrons is supposed to be determined by the reaction: normal atom $\rightleftarrows$ positive ion $+\nu$ electrons, which is governed by the ordinary laws of chemical equilibrium, and this gives for the specific electrical resistance $\rho = C(\nu N)^{-1/(\nu+1)}\, T^{a} e^{b/T}$, where ν is the valence in the reaction, N the concentration of atomic nuclei, $a = (\nu+4)/2(\nu+1)$, $b = (\varphi_0 - \psi_0)/(\nu+1)R$, $(\varphi_0 - \psi_0)$ being the mean energy required to bring about the hypothetical reaction of 0°K. This formula shows fair quantitative agreement with experimental data for both good and poor conductors; in particular, the constant a is about 1.25 for the alkali metals and less for metals of higher valence except in the case of Fe and Ni. For the metals the requirement is that φ_0 be slightly less than ψ_0 while for poor conductors φ_0 must be considerably greater than ψ_0. (2) *Interpretation of constant b in terms of photoelectric and thermionic work functions.* φ_0 and ψ_0 are identified with the photoelectric energy function and with the corresponding thermionic function respectively. According to the theory proposed the ordinary *expression for the thermionic saturation current* becomes: $i = BT^{(4\nu+1)/2(\nu+1)}\, e^{-\omega/RT}$, where $\omega = (\varphi_0 + \nu\psi_0)/(\nu+1)$ in the present notation. Therefore for metals the photoelectric φ_0 and the thermionic ω as experimentally determined should be practically identical, while for poor conductors the experimental φ_0 should considerably exceed ω. These conclusions are both in agreement with the facts. (3) *Explanation of photo-conduction.* This theory suggests that the mean value of φ_0 is diminished by absorption of radiation of the resonance frequency. For poor conductors this would bring about an increase in conductivity. While for metals at ordinary temperatures the conductivity would not be sensibly affected, at very low temperatures metals should prove photo-sensitive.

IN attempting to explain the electrical conductivity of good and of poor conductors the electron theory has so far required quite different methods of treatment. In the case of poor conductors like compounds and semi-metals Koenigsberger[1] found an expression for the specific resistance, the theory of which was based upon chemical dissociation of atoms into ions and electrons, the current in general being carried by electrons. In order to obtain close agreement with experiment it was necessary to include an empirical factor of the same form as appears in the temperature variation of metallic resistance. In recent work on

[1] Koenigsberger, Ann. der Phys. **32**, 179, (1910).

the conductivity of molybdenum sulphide,[2] a substance which may exhibit all phases between poor conduction and that of metals, the author attempted an interpretation of the behavior of this substance on the basis of Koenigsberger's theory, and found that the energy required to liberate a free electron from an interior atom on the average diminished considerably as metallic conduction was approached, an observation which led to the present paper. Probably the most successful theory to account for metallic conduction alone has been that of Bridgman,[3] in which the conductivity is given by the simple electron theory expression, with special assumptions in regard to the variation of the electronic mean free path, the concentration of free electrons being considered constant. It is the purpose of this article to show that, in an exceedingly natural and simple manner, it is possible to explain the temperature variation of electrical conductivity for both good and poor conductors on identically the same hypothesis for each. The theory proposed accepts the expression for the conductivity given by the simple electron theory, but like the theory proposed by Caswell[4] it assumes a constant or nearly constant mean free path, and explains conductivity variations by variations in the concentration of the free electrons. Like the theory of Koenigsberger it is based upon a chemical dissociation of atoms into ions and free electrons.

In the first place it is assumed that the electrons which may become free follow the ordinary laws of chemical equilibrium in their dissociation from the parent atoms. This assumes that the atmosphere of free electrons behaves like a perfect gas, i.e. that the mutual electromagnetic effects due to their charges are negligible. If we take as the simplest possible reaction $A \leftrightarrows A^+ + \epsilon$, where A is a neutral atom, A^+ a singly charged positive ion, and ϵ an electron, then the mass action law is $\log (C_+ \cdot C_\epsilon / C) = k$ where C, C_+ and C_ϵ are respectively the concentrations of atoms, ions and electrons in equilibrium. Now for this reaction, $C_+ = C_\epsilon = n$, the number of free electrons per unit volume; while $C = N - n$, where N is the total number of nuclei present in unit volume whether as neutral atoms or as ions.

Hence $\log [n^2/(N-n)] = k$

Solving for n, $n = \frac{1}{2}e^k(-1 \pm \sqrt{1+4Ne^{-k}})$

Therefore, if N is large compared with e^k;

$$n = N\tfrac{1}{2}e^k/2 \qquad (1)$$

[2] Waterman, Phys. Rev. **21**, 540, 1923.

[3] Bridgman, Phys. Rev. **17**, 161, 1921; **19**, 114, 1922.

[4] Caswell, Phys. Rev. **13**, 386, 1919.

This condition appears in general to be satisfied, except for the case of good conductors when quite near absolute zero.

The equilibrium constant k is given by

$$\partial k/\partial T = q/RT^2 \qquad (2)$$

where q is the average amount of energy required to bring about the reaction for a single atom.

In the case of a typical atom in its place in the solid structure, suppose the potential of the electron which may become dissociated is V_1 when held by the atom, and V_2 when free to take part in conduction. Roughly speaking then, V_1 may be the potential at the periphery of an atom, and V_2 the mean potential of the space through which the conducting electrons pass. Then $q=(V_1-V_2)\epsilon=\phi-\psi$. Thus ϕ is the energy required to remove a bound electron completely from the substance and V_1 is this ionization potential, presumably analogous to the ionization potential of a gas but not necessarily equal to it. Ψ is the energy required to liberate a free electron from the solid and is thus identified with the energy function ϕ dealt with in the theory of thermionic emission. By analogy with the behavior of gaseous atoms it is natural to assume that ϕ of the present theory is practically independent of the temperature. On the other hand ψ is expected by thermodynamical reasoning to vary with the absolute temperature as follows:[5] $\psi=\psi_0+(3/2)\ RT$, neglecting a relatively small term involving the specific heat of electricity.

Therefore we may write: $q=(\phi_0-\psi_0)-(3/2)RT$. Substituting this value of q in Eq. (2), and integrating:

$$k=-(\phi_0-\psi_0)RT-(3/2)\log T+\text{const.} \qquad (3)$$

where ϕ_0 and ψ_0 are independent of the temperature and characteristic of the substance and its structure.

Eq. (1) then becomes:

$$n=A\ N^{\frac{1}{2}}T^{-\frac{1}{4}}e^{-(\phi_0-\psi_0)/2RT}$$

where n is the number of free electrons per unit volume in equilibrium. In this expression the variation of N resulting from thermal expansion is neglected, as its effect on n is comparatively small.

The specific electrical conductivity σ which, according to the simple classical theory, is $\sigma=n\epsilon^2\lambda/2\sqrt{3mRT}$,

becomes $\sigma=A'N\ T^{-5/4}\ e^{-(\phi_0-\psi_0)/2RT}$

where $A'=A\epsilon^2\lambda/2\sqrt{3mR}$

or the specific resistance: $\rho=C\ N^{-\frac{1}{2}}T^{5/4}\ e^{(\phi_0-\psi_0)/2RT}$

In case a more general simple reaction is assumed for the liberation of electrons, of the form $A \leftrightarrows A^{\nu+}+\nu\epsilon$, where ν is the valence, by similar

[5] O. W. Richardson: "Electron Theory of Matter," p. 453.

argument (and using a similar approximation) the concentration of free electrons depends upon temperature as follows:

$$n=(\nu N)^{1/(\nu+1)}\, e^{k/(\nu+1)}=A\,(\nu N)^{1/(\nu+1)}\, T^{-3/2(\nu+1)}\, e^{-(\phi_0-\psi_0)/(\nu+1)RT} \tag{4}$$

whence $$\sigma=A'(\nu N)^{1/(\nu+1)}\, T^{-(\nu+4)/2(\nu+1)}\, e^{-(\phi_0-\psi_0)/(\nu+1)RT} \tag{5}$$

and $$\rho=C(\nu N)^{-1/(\nu+1)}\, T^{(\nu+4)/2(\nu+1)}\, e^{(\phi_0-\psi_0)/(\nu+1)RT} \tag{6}$$

where $$C=2\sqrt{3mR}/A\,\epsilon^2\lambda$$

It is seen that the theory requires that the valence of an element should influence its conductivity. Thus for a

univalent reaction: $(\nu=1)$, $\rho \propto T^{1.25}e^{(\phi_0-\psi_0)/2RT}$;

bivalent reaction: $(\nu=2)$, $\rho \propto T^{1.00}e^{(\phi_0-\psi_0)/3RT}$;

trivalent reaction: $(\nu=3)$, $\rho \propto T^{0.875}e^{(\phi_0-\psi_0)/4RT}$;

quadrivalent reaction: $(\nu=4)$, $\rho \propto T^{0.800}e^{(\phi_0-\psi_0)/5RT}$; etc.

In any case the dependence of the specific resistance upon temperature is of the form:

$$\rho=CT^a\, e^{b/T} \tag{7}$$

where C, a and b are constants characteristic of the substance.

Now an examination of conductivity data shows that in general the temperature variation of specific resistance (at constant e.m.f. and pressure) for all solid conductors (with the possible exception of alloys) may be represented quite approximately by an expression of this type, Eq. (7).

For the best conductors, i.e. metals, a is of the order of magnitude of unity, and b/T is small at ordinary temperatures so that the exponential factor is nearly unity. At low temperatures better agreement is shown if b is negative, since the specific resistance then approaches zero exponentially as the temperature diminishes. In the theoretical expression it is seen that the exponent of T does approximate unity for all valences, while the requirement for metals that b should be small and negative may be met by assuming that ϕ_0 is slightly less than ψ_0.

For poor conductors, such as Se, B, and many compounds, the constant b is large and positive, so that the factor T^a has little effect, and the specific resistance of these solids at all available temperatures decreases exponentially with rising temperature. Thus for such conductors ϕ_0 is much greater than ψ_0.

For transitional substances such as Si, Ge, and some compounds, which show a minimum resistance, preceded by the characteristics of poor conductors and followed by metallic conduction, b, i.e. $(\phi_0-\psi_0)$, has an intermediate positive value and a is in the neighborhood of unity. As a matter of fact the theoretical expression predicts a minimum resistance at a temperature given by:

$$T=2(\nu+1)\,(\phi_0-\psi_0)/(3\nu+4)R$$

Thus there is no minimum resistance (except at 0°K) when ϕ_0 is less than ψ_0, the case of metals. For poor conductors, where ϕ_0 is much larger than ψ_0, the temperature of minimum resistance would be impossibly high or above the melting point. Changes of structure such as polymorphic transitions involve a change in the constants of the expression and offer no difficulties.

TABLE I

Element	Valence	Obs. Exponent a' in $\rho \propto T^{a'}$	Range of Exp. Data (°C)	Constancy of a' fails
Li	I	1.30	−187 to 100	
Na	I	1.34	−200 to 93.5	below −150
K	I	1.33	−200 to 60	below −100
Rb	I	1.29	−190 to 35	
Cs	I	1.3	−187 to 27	
Ca	II	1.0	0 to 100	
Sr	II	1.0	0 to 100	
Cu	I, II	1.15	−259 to 1083	below 0
Ag	I	1.10	−259 to 960	below −150
Au	I, III	1.12	−253 to 1063	below −150
Mg	II	1.07	0 to 100	
Zn	II	1.15?	−253 to 415	below −150
Cd	II	1.02	−253 to 300	below −100
Hg	I, II	1.20	−200 to −50	below −150
Sn	II, IV	1.1	−200 to 225	below −100
Pb	II, IV	1.09	−253 to 200	below −200
Al	III	1.22	−190 to 400	
Tl	I, III	1.13	−183 to 100	below −100
Bi	II-V	0.91	−200 to 259	above 20
		mean		
Fe	II, III	1.43	−253 to 400	below −100
Ni	II, III	1.45	−180 to 100	
W	II-VI	1.24	0 to 2000	
		1.0	0 to 100	
Rh	III, IV	1.13	−186 to 100	below −80
Ir	III, IV	0.99	−180 to 100	
Pd	II, IV	0.95	−183 to 100	below 0
Pt	II, IV	0.96	−264 to 1600	below −73 above 1000

In the case of metallic conductors the extent of the quantitative agreement with experimental data is shown in the Table. The theoretical formula for this case is $\rho = CT^a e^{-b/T}$, expressing explicitly the fact that b is here negative. By plotting logarithmically the experimental values for specific resistance against absolute temperature, the slope of each curve at any point according to the theory should be: $a' = a + b'/T$, where $b' = .434\ b$, common logarithms being used. Thus the observed slope a' should exceed the theoretical exponent a by an amount

$b'T$. At ordinary temperatures or higher, b'/T is expected to be small if not negligible; consequently in this region the observed slope a' should be nearly constant and show a variation with valence from element to element similar to that of the theoretical temperature exponent a. At low temperatures on account of the additive term b'/T the observed slope a' should considerably exceed a and should increase rapidly with diminishing temperature. The approximate temperature at which the constancy of a' thus fails is given in the fifth column. The experimental data are taken from the Smithsonian Physical Tables, with the exception of the short range observations (0° to 100°C) which are Bridgman's.

For the alkali metals, for which a univalent reaction $A \leftrightarrows A^+ + \epsilon$ may with most confidence be assumed, the experimentally determined temperature variation of resistance shows striking quantitative agreement with the theory. The observed slope a' is nearly the same for all metals of this group, and exceeds the theoretical exponent a by 3 to 7 per cent, which is entirely consistent with the theory, while the customary first power of the absolute temperature is wrong by 29 to 34 per cent. Na and K show a marked departure from constancy of a' at the lowest temperatures given, which would be due to the effect of the exponential factor of the formula.

For the alkaline-earth metals Ca, Sr and Ba, the bivalent reaction alone would be expected to occur or certainly to predominate, for which a first power of the absolute temperature should be exact. The results as far as they go are in entire accord with the theory, i.e., $a = 1.00$. It is unfortunate that a greater range of temperature has not been studied and that Ba seems not to have been investigated.

A priori it appears far from certain that the reaction of an atom of a solid in liberating electrons should necessarily be governed rigidly by the valence which that atom exhibits in forming chemical compounds, except in the case of the alkali metals. Rather it seems quite likely that an atom should behave somewhat after the manner of a gaseous atom, where in general ionization may take place progressively, i.e., $A \rightarrow A^+ + \epsilon$, $A^+ \rightarrow A^{++} + \epsilon$, etc., until the possible number of free electrons is exhausted, a stage which will depend upon the highest possible valence. The ionization potentials will in general be different for each dissociation and characteristic of the atomic structure. Thus intermediate values of a will in general be expected, and especially where more than one chemical valence exists. But it seems also possible that in the solid state one or more of the outer electrons may in certain cases be strongly held in place as a bond of union between adjacent atoms and thus be

prevented from becoming free. Or on the other hand the atomic structure might possibly be altered in such a direction as to facilitate the liberation of additional electrons. Thus there would appear to be two factors which may be operative in any such atomic dissociation within a solid, the atomic structure of the individual atom, and the interatomic or molecular structure.

With these considerations in mind, the agreement is seen to be good on the whole, between the experimental and the calculated data in the case of the other metals listed. It will be noted that the observed values of a' are in most cases somewhat greater than the theoretical values of a, as would be expected for the several reasons given. The valence in the conductivity reaction is distinctly different from the ordinary chemical valence for Ag, Al, W, Fe and Ni. In the case of Al and W the former valence is lower, and thus it seems that a much greater amount of energy is required to free a second electron than the first, the reason for which may lie in the nature of the interatomic structure as suggested. Ag is a surprise, with an apparent reaction which is partly bivalent. This is not so serious an exception as would be the case if one of the alkali metals showed other than a univalent reaction. Also, according to the most recent developments of the Bohr-Sommerfeld theory, the atomic structures of Cu and Ag are almost exactly similar, so that the nearly identical behavior in conductivity of these two elements, including the same type of reaction liberating electrons, would be expected. From this point of view the surprise is that Cu and Ag differ in chemical valence. Incidentally it may be mentioned that according to the Bohr-Sommerfeld theory the three valency electrons of Al are distributed with one alone in the outermost highly eccentric orbit, and two in the next orbit of smaller eccentricity. Thus there is some basis for the fact that Al appears to be univalent in its conductivity reaction. The two similar metals Fe and Ni are outstanding exceptions to the theory in its present form, and for these no explanation is offered at present, except a suggestion that these two may have a sort of molecular dissociation of the form $2A \leftrightarrows (2A)^+ + \epsilon$, for which a should be 1.50. The strongest support from experimental data comes from the case of the alkali metals, where a univalent reaction appears absolutely necessary, and where an exclusive univalent reaction is found in fair agreement.

Incidentally a characteristic of the experimental graphs in many cases was found to be a slight increase in the value of a' on approaching the melting point, which was most pronounced in the case of Bi. Pt was a notable exception where a decrease occurred.

Fig. 1 shows the graphs of specific resistance vs. absolute temperature, plotted logarithmically in the manner in which the slopes a' were obtained, for three representative metals, Na, Cu and Pt. It will be seen from the Table that Cu and Pt might be expected to give trouble, inasmuch as the constancy of the observed slope a' fails below a higher temperature than for most metals. The curves drawn represent the theoretical variation of resistance according to Eq. (7). For the Na curve the theoretical value $a=1.25$ was assumed and the agreement

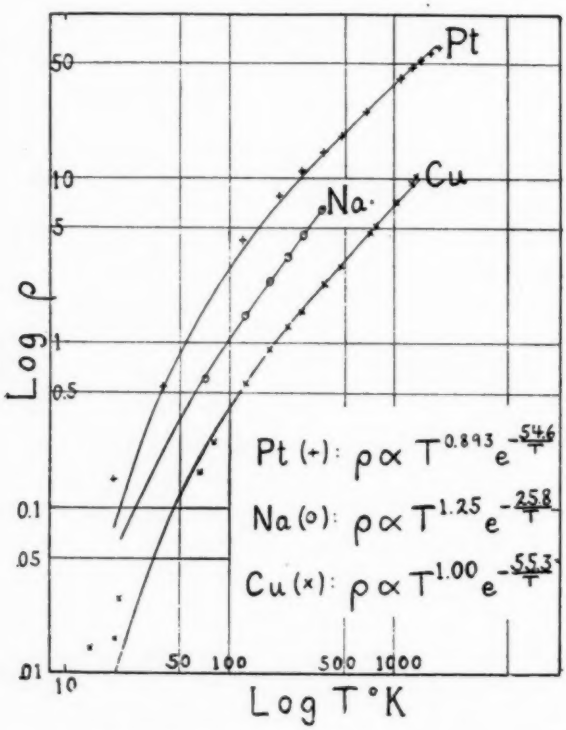

Fig. 1. Specific resistance as a function of absolute temperature.

is excellent. For Cu and Pt no exact value of the theoretical exponent a could be predicted, so that the curves merely represent the theoretical expression with a choice of constants which approximates the observed behavior. It is observed that at the lowest temperatures for Cu and Pt a departure from agreement occurs. It is in this region however that the approximation underlying the expression (7) might be expected to break down. Better agreement here could be obtained with a more rigorous expression, as higher values of the resistance would then be obtained.

On the basis of this theory super-conductivity might possibly be accounted for by a polymorphic transition, which as readily seen in such changes at ordinary temperatures involves a change in the difference $\phi_0 - \psi_0$.

It is hardly necessary to give data to show agreement with experiment in the case of poor conductors, as the theoretical expression here derived is of the same type as that of Koenigsberger[1] with T^s substituted for the factor $(1+\alpha t+\beta t^2)$. Taken empirically there is practically no choice between these two factors, especially when the order of accuracy of experiments with poor conductors is considered. The expression also compares favorably with Bidwell's[6] empirical formula for transitional substances. In this formula the "metallic resistance" factor is assumed to be e^{xT} instead of T^s.

It is interesting to consider the physical interpretation of the quantities ϕ_0 and ψ_0. On the basis of this theory the behavior of metals at low temperatures is explained by the hypothesis that ψ_0 is slightly greater than ϕ_0. Thus the space in which the conducting electrons travel in metals is at a higher potential than that of their normal positions when held by the atom. This may be considered to point to the conclusion that for metals the conducting electrons pass chiefly through the interiors of the atoms rather than to any extent through a real space between them, a result which is in agreement with the view of Bridgman for most metals. On the other hand in the case of poor conductors, the fact that for these substances ϕ_0 is greater than ψ_0 may indicate that the conducting electrons traverse mainly the interatomic space.

The theory derives additional confirmation in an entirely different direction. As has been stated the function ψ_0 should be identical with the theoretical thermionic function commonly denoted by ϕ_0. Suppose the function ϕ_0 of the conductivity expression to be identified with the corresponding energy function ϕ_0 in the theory of photoelectric emission. This interpretation is equivalent to assuming that thermionic emission involves directly only the free electrons while photoelectric emission affects directly only the electrons bound by the atom. Although the correctness of this view of photoelectric emission is still debated it is on general principles the most natural assumption to make, and is consistent with the fact that photoelectric emission seems to be independent of the temperature.

This interpretation makes possible a consideration of the experimental values obtained for the thermionic and the photoelectric energy functions in connection with the theoretical expression for the conductivity.

[6] Bidwell, Phys. Rev. **29**, 447, 1922,

It is first necessary to point out that the ordinary expression for the thermionic current, namely:

$$i = B'T^2 e^{-\omega/RT} \tag{8}$$

(using ω, to avoid confusion, in place of the usual notation ϕ_0) should be modified. This equation is obtained from:

$$i = BnT^2 e^{-\psi_0/RT}$$

with n, the concentration of free electrons, considered constant, and thus becomes:

$$i = B''\ (\nu N)^{1/(\nu+1)}\ T^{[2-3/2(\nu+1)]}\ e^{-[\psi_0/RT+(\phi_0-\psi_0)/(\nu+1)RT]},$$

since n varies with temperature according to equation (4), or

$$i = B''\ (\nu N)^{1/(\nu+1)}\ T^{(4\nu+1)/2(\nu+1)}\ e^{-(\phi_0+\nu\psi_0)/(\nu+1)RT} \tag{9}$$

which for a univalent reaction would be: $i = B''N^{\frac{1}{2}}T^{5/4}e^{-(\phi_0+\psi_0)/2RT}$.

Thus according to the theory the experimentally determined values of the thermionic energy function ω in equation (8) are in reality values of $(\phi_0+\nu\psi_0)/(\nu+1)$ rather than ψ_0. Now in the case of metals the conductivity expression (5) indicates that ϕ_0 and ψ_0 are nearly equal, and therefore the experimental values of ϕ_0 and ω should prove also nearly equal. Although the consistency of such determinations of ϕ_0 and ω has been far from satisfactory the fact is that both appear to be closely of the same magnitude for metals. The maximum difference may even be roughly predicted from the conductivity data. Thus the probable maximum value of $(\phi_0-\psi_0)/(\nu+1)R$ in the case of any metal appears to be in the neighborhood of 100°. An approximate calculation shows this to result in a difference between ϕ_0 and ω of less than 1 per cent, the latter being greater. This is a crude maximum difference for the most favorable case; the difference would be expected to be considerably less for most metals. For example, taking the experimental value of the thermionic energy function for Na as 1.82 equivalent volts in conjunction with the value of b $(=(\phi_0-\psi_0)/2R)$ from the conductivity data (cf. Fig. 1), namely $-51.6°$, whence $\phi_0-\psi_0=-4.5(10)^{-3}$ equivalent volts, it follows that $\phi_0=1.82-0.002$ equivalent volts. Therefore the difference between the photoelectric function ϕ_0 and the thermionic ω should escape experimental detection by direct methods used thus far.

It should prove extremely interesting to compute in this manner the difference between ϕ_0 and ψ_0 from the conductivity data for many elements. Unfortunately the experimental data for specific resistance over a wide range of temperature, and especially at low temperatures, are in general neither extensive nor consistent enough for this purpose. A most satisfactory beginning in such study could be obtained if data were available for all the alkali and alkaline-earth metals in solid form

of highest purity, since for these metals the valence in the hypothetical conductivity reaction would be definitely known. It is important for the sake of consistency in results that the *same specimen* be observed over the entire range of temperature available, and that especial attention be paid to observations at the temperature of liquid air and below. Another and more complex method of attack would be further systematic and careful investigation of the specific resistance of poor conductors over large ranges of temperature, with especial attention to points of minimum resistance, and to polymorphic changes.

In the case of poor conductors like the oxides and sulphides the conductivity expression indicates that ϕ_0 is much larger than ψ_0. It follows that the observed values of ϕ_0 should be considerably greater than ω. This again is found to be the case for such conductors. For example Hughes[7] gives $\phi_0 = 5.0$ and $\omega = 1.9$ equivalent volts in the case of CuO. If for the liberation of electrons within the oxide a bivalent reaction is assumed as being the predominating type and especially as approximating the reaction for metallic Cu, then since $\omega = (\phi_0 + 2\psi_0)/3 = 1.9$, $\psi_0 = 0.35$ equivalent volts. Hence $\phi_0 - \psi_0 = 4.65$ and the specific resistance of CuO should be proportional to $Te^{(\phi_0 - \psi_0)/3RT}$ or $Te^{18,000/T}$, which would indicate a low conductivity and a rapid exponential decrease in resistance with rise in temperature. The experimental values for ϕ_0 and ω are subject to far too much uncertainty for such numerical computation, however; indeed, if the theory is correct, more accurate comparative values of ϕ_0 and ω should be obtained by aid of the conductivity data.

The theory also affords a natural explanation of increase in conductivity under the influence of light. The explanation generally offered is that the increased conductivity is due in part at least to the presence of photoelectrons within the substance. This explanation, if correct, may be sufficient on any theory, but it encounters difficulties. In the present theory, if the analogy holds between solid and gaseous atoms, we might expect to find the ionization energy or potential of any atom affected by absorption of radiation of the resonance frequency. The effect of such absorption would be to diminish the mean value of ϕ_0, and in consequence for the case of poor conductors where $\phi_0 - \psi_0$ is a large positive difference and the exponential factor most important, the conductivity should increase. This view has already been advanced by the author in explanation of the light sensitiveness of molybdenite.[2] For metals, the exponential factor being nearly negligible at ordinary

[7] Hughes (after Millikan and Richardson), Bulletin of the National Research Council, Vol. 2, Part 2, No. 10.

temperatures, the conductivity would not be sensibly affected unless the value of ϕ_0 were greatly altered. But if this hypothesis concerning light-sensitiveness and the proposed explanation of conductivity at low temperatures are correct it follows that metals should be found light-sensitive at very low temperatures. It should be noted that this explanation of light-sensitiveness does not require an emission of photoelectrons caused *directly* by the radiation, but only that the absorption of radiation diminishes the mean amount of energy required to liberate an electron, and the equilibrium condition then necessitates an increased concentration of free electrons. This may also explain why photo-conductivity for a given substance is more readily produced than photoelectric emission from the surface.

Unless the constant of integration in Eq. (3) is evaluated by some independent method, it is impossible to compute the actual concentration, mean free path, etc. of the free electrons. With this constant at our disposal, the conductivity formula given is consistent with any values of the mean free path and concentration, as for instance Bridgman's, which do not make the concentration approach that of the atomic nuclei too closely, since when n is of the same order of magnitude as N the approximation underlying the simple conductivity formula is invalid. In regard to the variation of the mean free path λ with temperature possibly the most natural assumption is that λ varies as the mean distance between adjacent nuclei or as the inverse third power of the concentration of nuclei. As this latter concentration enters into the conductivity formula independently in the factor $(\nu N)^{1/(\nu+1)}$ it is seen that not only is the variation produced by thermal expansion quite small in either factor, but the effect on λ is always nearly offset by the direct effect on N.

It is apparent that a conductivity theory of the form here outlined possesses singular advantages in its ready application and extension to numerous allied effects. Further investigation along these lines is now in progress.

I wish to express my thanks to Professors K. T. Compton and Leigh Page for helpful criticism and suggestions.

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MAGNETOSTRICTION AND MAGNETOELECTRIC EFFECTS IN IRON, NICKEL AND COBALT

By Paul McCorkle

Abstract

Magnetostriction effects in pure cobalt and in iron and nickel.—Various properties of the same sample of very pure cobalt wire (Co 99.73 per cent) annealed at 1100°C were determined and compared with those of Armco iron and commercially pure nickel. (1) *Wiedemann effect.* As found by Pidgeon, Co is intermediate between Fe and Ni, the twist for 6 amp./mm² decreasing to a minimum of 21 sec./cm for a field of 50 gauss. (2) *Joule effect* in longitudinal field for Co is also intermediate between Fe and Ni, $\Delta L/L$ decreasing steadily to -20×10^{-6} for 1000 gauss. For Fe, as has usually been found, the effect was positive only up to 250 gauss.

Magnetoelectric effects in pure cobalt and in iron and nickel.—(1) *Change of thermal e.m.f.* in longitudinal field. $\Delta E/E$ was positive for Fe, reaching a maximum of .021 for 110 gauss; for Ni, it was negative, increasing to $-.026$ for 1000 gauss; for Co, it was intermediate, reaching a maximum of only 5×10^{-4} and being negative above 300 gauss. The effect of loading Fe and Ni was to lower the curves considerably in the negative direction; for Co, the effect was less. (2) *Change of resistance* in longitudinal field. For Fe, $\Delta R/R$ increased to a constant value 2×10^{-3} for $H>800$ gauss; for Ni, it increased rapidly to a steady value 14.8×10^{-3} for $H>400$ gauss; for Co, the values were intermediate, increasing steadily to 4×10^{-3} for 1000 gauss.

BECAUSE of the importance of magnetostrictive and magnetoelectric effects in theories of magnetism, it is desirable that all these effects be studied carefully in the same specimen. The importance of such observations has already been pointed out by Williams[1] who emphasizes the fact that differences in purity and in the previous history of the specimens makes the coördination of the results of various observers difficult. The disagreement in this respect is illustrated by the work of Heaps,[2] who found that a longitudinal magnetic field produces a contraction in iron for all values of the magnetic field, but all other observers, except in the case of one determination by Bidwell, found an elongation in weak fields and a contraction in strong fields. Unfortunately, no analysis was given of the specimen used by Heaps.

These effects have received comparatively little attention in the case of cobalt, largely because of the difficulty of securing suitable specimens.

[1] Williams, Phys. Rev. **10**, 129, 1917.
[2] Heaps, Phys. Rev. **6**, 34, 1915.

Among those who have studied cobalt are Honda and Nagaoka,[3] Goldhammer,[4] Bidwell[5] and Pidgeon.[6] In most of these cases mention is made of the fact that the annealing was imperfect and the specimen impure. Fortunately a careful study of cobalt has been made for the Bureau of Mines in Canada under the direction of Eugene Haanel at the School of Mining at Queen's University. This study resulted in the production of a very pure metal which could be drawn into the form of wires. A specimen of this wire previously used by Pidgeon was available for this work. Its analysis was as follows: Co = 99.73, Fe = .14, Ni = .00, S = .01, C = .09, and Si = .02 per cent.

Neither the specimen of iron nor that of nickel has been analyzed as, in view of the immense amount of work done on iron and nickel specimens in the past, it did not seem necessary. The former was pure Armco; the latter was labelled pure nickel by the Driver Harris Co.

The dimensions of the specimens were:

	Length	*Diameter*
Cobalt	22.3 cm	0.88 mm
Nickel	17.0 cm	1.25 mm
Iron	25.0 cm	1.02 mm

The cobalt was annealed at 1100°C in a chromel resistance furnace for two hours, with hydrogen flowing through the furnace. The specimen was then slowly cooled to room temperature and found to be fairly flexible. Annealing at a temperature lower than 1100° C left the metal quite stiff. The iron and nickel specimens were annealed at 950°C for two hours and then cooled slowly. At the end of this treatment they were soft and flexible.

The Wiedemann Effect

The solenoid used in the work on the Wiedemann effect in iron was one built at the Carnegie Institute of Technology by Grondahl.[7] It had a calculated constant of 122.5 gauss per ampere. Since it was wound with No. 8 wire, large currents could be used for short intervals without heating. For the remainder of the work a second coil was wound with No. 12 wire. Its constant, carefully determined by two independent methods, was 110 gauss per ampere. The solenoids were sufficiently long so that the fields were uniform to about two per cent over a length of 25 cm in the center. A layer of fine wire wound on the outside of the coil

[3] Honda and Nagaoka, Phil. Mag. **4**, 45, 1902.
[4] Goldhammer, Wied. Ann. **31**, 360, 1887.
[5] Bidwell, Roy. Soc. Proc. **48**, 469, 1890.
[6] Pidgeon, Phys. Rev. **13**, 209, 1919.
[7] Grondahl, Phys. Rev. **4**, 325, 1914.

served to compensate the vertical component of the earth's magnetic field. Since the solenoid was always used in the vertical position no compensation was made for the horizontal component.

For work on the Wiedemann effect the specimen was supported between two brass rods and was surrounded by a cooling tube through which water ran continuously. The specimen was fixed to a bracket on a pillar separate from the building. Even with this precaution, the vibrations of the building caused trouble especially in the case of cobalt.

The method for the measurement of the Wiedemann effect was that used by Pidgeon.[6] It was necessary to compensate carefully for the earth's magnetic field, especially in the case of nickel. Pidgeon found that a small twist resulted when he used only one of the two fields. This was nearly all eliminated by careful compensation. The small residue may be due to aeolotropy in the material.

In the case of iron nothing was found at low fields that was not already well known, but on carrying the fields to high values it was found that

TABLE I

Soft iron I_c 2.7 *amp./mm²*		*Nickel* I_c 2.38 *amp./mm²*		*Cobalt* I_c 6.00 *amp./mm²*	
H(gauss)	*θ(sec./cm)*	*H(gauss)*	*θ(sec./cm)*	*H(gauss)*	*θ(sec./cm)*
2.8	5.4	3.2	41.7	4.3	1.3
4.0	7.7	4.0	55.5	8.5	3.8
5.2	10.2	4.8	58.5	19.3	9.0
5.8	14.0	5.6	66.1	35.4	17.7
6.9	17.1	6.4	76.0	50.2	20.5
8.7	21.0	7.2	76.5	72.0	17.0
11.0	25.0	8.0	86.0	85.4	13.8
15.2	26.7	10.4	86.0	105.2	10.2
25.5	24.4	11.2	90.5	168.2	5.2
63.5	16.6	16.0	89.5	240.3	3.1
113.2	5.5	22.7	79.5	400.2	2.0
158.0	3.02	36.0	66.3	570.2	1.9
207.2	1.72	72.0	36.5	860.3	1.9
253.0	1.16	101.8	28.5	1230.5	1.8
300.5	0.29	140.0	20.5		
335.2	− .75	168.2	18.2		
382.0	−1.16	207.0	14.6		
430.0	−1.46	233.3	13.2		
464.3	−1.56	273.5	11.9		
497.6	−1.86	327.8	9.9		
695.0	−2.6	344.2	7.3		
1160.4	−4.3	815.4	3.3		
2080.2	−5.8	1230.0	0.66		
		2080	0.5		

NOTE. The negative sign in the case of iron means negative twist. In the case of nickel and cobalt all the twists are in the negative direction. Fewer readings were taken on cobalt owing to the danger of heating by the high current used and a consequent change of structure. The data taken by Pidgeon on the same specimen seem to agree very well with the results of the author, so that only a limited number are given in the paper.

the twist in the opposite direction, which we shall call negative,* did not tend to return to the axis of zero twist as found by Pidgeon, but continued to increase negatively up to the highest fields used, about 2500 gauss. In both Fig. I and Table I, I_c is the current flowing in the specimen.

A sample of electrolytic iron, furnished through the kindness of Mr. Hopkins of the Westinghouse Mfg. Co., was given the same heat treatment as the other sample of iron, and was found to have the same general characteristics as the Armco iron. Twists in it (Fig. 2) were very steady and easily reproduced.

In nickel (Fig. 1) the usual type of twist was found. It is negative for small fields, reaches a maximum and then approaches the axis of zero twist for high fields. In the largest fields used the twist was very nearly zero.

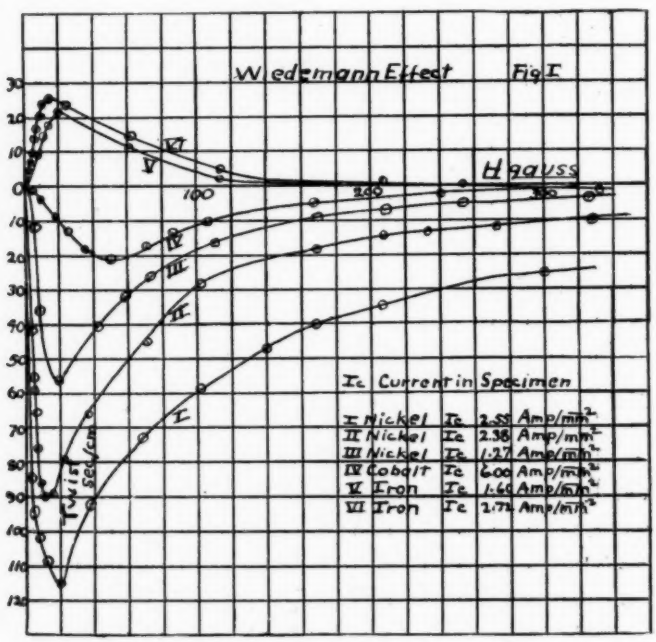

Fig. 1. Wiedemann effect.

The results for cobalt (Fig. 1) confirmed those obtained by Pidgeon on the same specimen. They are consistently intermediate between iron and nickel. This suggested the investigation of other effects to see whether this was always true.

* The convention of positive twist is that for iron at low fields when the lower end of the solenoid is a north pole, and the current is flowing from top to bottom of the wire.

The Joule Effect

This effect, the change in length with magnetic field, has received much attention in the case of iron and nickel. The results obtained for cobalt by various observers have not been consistent. Bidwell found that cobalt first decreases in length in low magnetic fields, then reaches a mini-

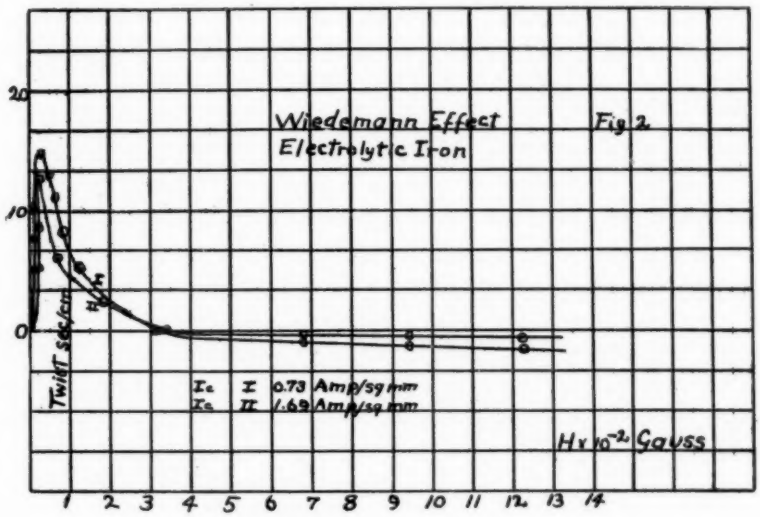

Fig. 2. Wiedemann effect in electrolytic iron.

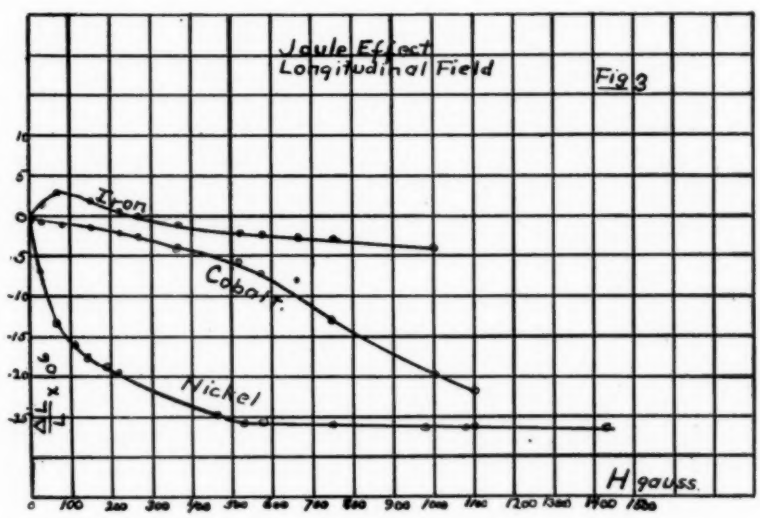

Fig. 3. Joule effect with longitudinal field.

mum and finally increases in length as higher fields are reached. Honda found a continual decrease in length.

Two methods were used to measure this effect. One was the bifilar method described by Grondahl. The other was an optical lever method which consisted in the combination of a first class lever with an optical lever. The distance between the front and back legs of the optical lever was 3 mm, and the telescope and scale were placed 4 meters away. This combination gave a magnification of 30,150. An attempt was made to carry this magnification higher but vibrations interfered.

The results reported here (Fig. 3) show that in cobalt there is a continual decrease in length. It is small for low fields, but reaches no maximum in the fields used in these experiments. Disregarding the small increase in length in iron for low fields, the Joule effect is always negative; with cobalt it is intermediate between iron and nickel. A careful study of the change in length in cobalt for magnetic fields less than 100 gauss was made, to see if there might be a small increase in length at low fields. Nothing of this character was found with the magnification used.

The usual initial increase in length was found consistently in iron. The result obtained by Heaps—a contraction for all magnetic fields—was not observed.

Change of Thermal Electromotive Force

In the determination of the change of thermal electromotive force in a longitudinal magnetic field a Wolff potentiometer was used with a Leeds and Northrup high sensitivity galvanometer. The accuracy of the potentiometer was checked frequently with a Weston cell. The sensitivity of the galvanometer at 3 meters was 6.07 mm per microvolt. The junctions which were formed by soldering the ends of the specimens to copper wires, were kept in melting ice and steam. It was found difficult to keep the temperature of the ice junction constant but by drawing off the water frequently, the zero of the galvanometer could be maintained for several minutes.

This change of thermal electromotive force in pure ductile cobalt was of added interest because Smith[8] has studied it in iron, nickel and a number of alloys, and Grondahl and Karrer[9] had observed this change in a bar of cast cobalt. The results (Fig. 4) show an increase to a maximum for iron in low fields. This is followed by a decrease in high fields. It is unfortunate that this effect was not studied by Heaps, as there is a

[8] Smith, Phys. Rev. **19**, 285, 1922.
[9] Grondahl and Karrer, Phys. Rev. **33**, 531, 1911.

possibility that the sample used by him might have shown a continual decrease. Nickel increases in the opposite direction and seems to approach a maximum. These results are very similar to those obtained by Smith. Cobalt shows a small change in low fields in the direction of iron. In higher fields the change is in the direction of nickel as one should expect from the direction of the Peltier effect in a copper cobalt junction. The curve of Grondahl and Karrer does not show the initial change. Cobalt is again intermediate between iron and nickel.

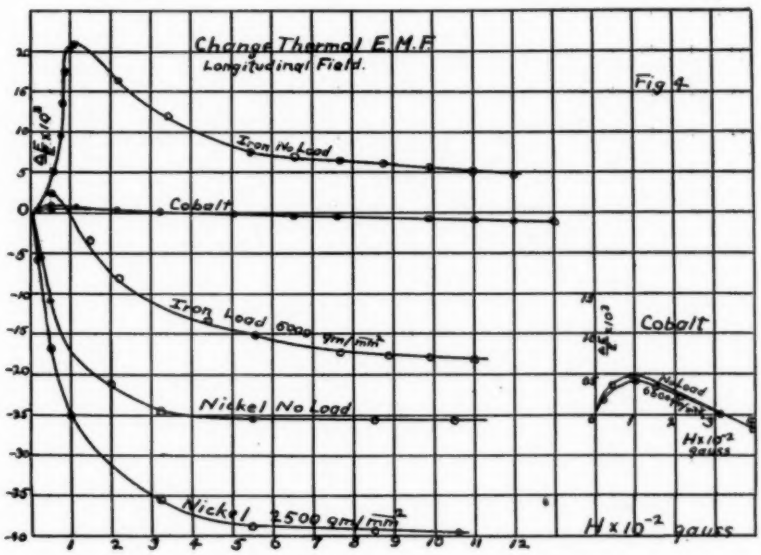

Fig. 4. Change of thermal e. m. f. with longitudinal field.

In this connection the effect of loading the specimen with weights was tested. The results are in agreement with those found by Smith. Cobalt behaves like iron in this respect. For the small loading used in the case of cobalt the curves did not vary much at high fields. This deserves further study as small loads were used in order to avoid risk of setting up any internal changes in the structure of the specimen.

Change of Resistance

The change of resistance in a longitudinal magnetic field was measured on a Kelvin double bridge with a Leeds and Northrup high sensitivity galvanometer. A change of 1×10^{-5} ohm could be detected. The bridge was equipped with a sliding contact for a null method which was found very satisfactory. A deflection method was tried and the results were the same in both cases. To correct for possible thermal electromotive

forces set up at the contact, the current was reversed in the bridge for each reading. The mean of the two readings differed little from either reading. Because the resistance of the specimens never exceeded 0.04 ohm there was small danger of change of resistance due to the heating of the specimen. Nevertheless water at constant temperature was kept constantly running through the cooling tube and the readings were taken as rapidly as possible to avoid error. It was evident that very little change took place as the initial resistance remained practically constant during the series of runs.

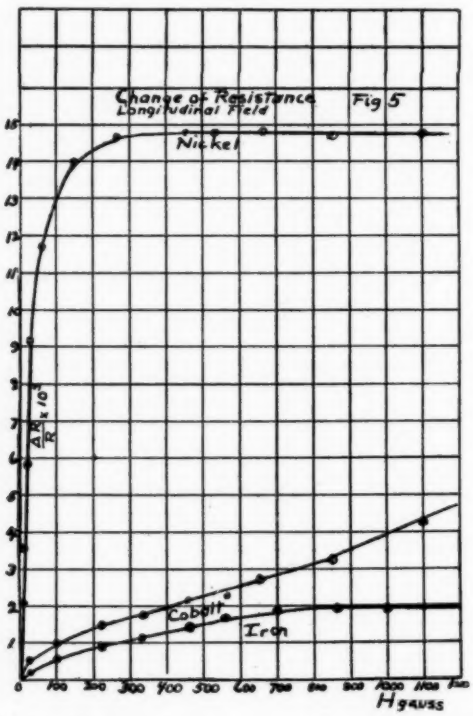

Fig. 5. Change of resistance with longitudinal field.

The results for iron and nickel are in agreement with those of other observers. In the case of cobalt (Fig. 5) an increase of resistance intermediate between those of iron and nickel was found. In each case, then, the effect for cobalt is intermediate between those for iron and nickel, in agreement with the order of the atomic numbers of the three metals.

ROCKEFELLER HALL,
CORNELL UNIVERSITY,
March 19, 1923.

THE MEASUREMENT OF MAGNETIC FIELDS OF MEDIUM STRENGTH BY MEANS OF A MAGNETRON

By Albert W. Hull

Abstract

Use of magnetron to measure magnetic fields of strength 0.1 to 500 gauss.—The magnetron is a special symmetrical type of kenotron, with a straight axial filament and cylindrical anode. When this is placed in a magnetic field parallel to its axis, the radial paths of the electrons are curved into arcs of circles, and for fields stronger than the critical for the given voltage, do not reach the anode at all; or, for a given field, as the voltage is decreased, the current suddenly begins to decrease rapidly at a critical voltage. *Two methods* are described. (1) The magnetron is connected in series with a high resistance and a source of voltage, and in parallel with a standard voltmeter. Then for a field H at the center of the magnetron, parallel to its axis, there is a definite reading V of the voltmeter, given by the equation $H=6.72\ V^{\frac{1}{2}}/R$, when R is the radius of anode. This method may be used for 20 to 500 gauss. (2) For weak fields, $H<20$ gauss, the magnetron is connected in series with a milliammeter, (which may be the voltmeter used in (1) with its resistance short-circuited) and a source of voltage, and surrounded by a close-fitting solenoid. The solenoid is connected, through tungsten filament lamps, to the same source of voltage as the anodes, and the lamp resistance adjusted so that the magnetic field of the solenoid is the "critical" field of the magnetron. The combination of magnetron and solenoid is then calibrated, and the calibration is found to be practically independent of voltage fluctuations. The accuracy of the first method is $\frac{1}{4}$ per cent with calibration or for relative values over a small range without calibration, using commercial power supply and portable meters. The accuracy of the second method is about 1 per cent under good conditions.

Introduction

ALL methods in use at the present time for measuring magnetic fields of weak or medium intensity have two practical limitations: (1) They require a delicate, non-portable current measuring instrument; (2) they measure the effect of a *change* of field, not the field itself. Hence, it is necessary either to vary the field that is to be measured, as by annulling or reversing, or to move the measuring coil with respect to the field. In the majority of cases the field is due in part to magnetism in iron, and cannot be varied in a known manner, so that the movement of the coil is the only practical method.

The method here described is free from these limitations. The measurements can be made with a standard portable voltmeter, without

motion or variation of field, and with an accuracy fully equal to that of the galvanometer methods.

The Magnetron

All electron tubes, especially those of the high vacuum type, are susceptible to the influence of magnetic field. Any such tube could therefore be used, with proper calibration, for the measurement of magnetic field intensity. In general, however, the effect of the field depends on the construction and orientation of the tube in a way that is not easily specified, so that careful precautions would be necessary in operation. These precautions are unnecessary when a symmetrical tube of the type here described is used. Even calibration may be dispensed with, except when great accuracy is desired. In addition, it becomes possible to extend the measurements to fields much weaker than can be detected with ordinary tubes.

The magnetron has been fully described elsewhere.[1] It is a special form of two-electrode kenotron, whose cathode is a straight filament, and whose anode is a circular cylinder concentric with the cathode (Fig. 1). The effect of a magnetic field parallel to the cathode is as fol-

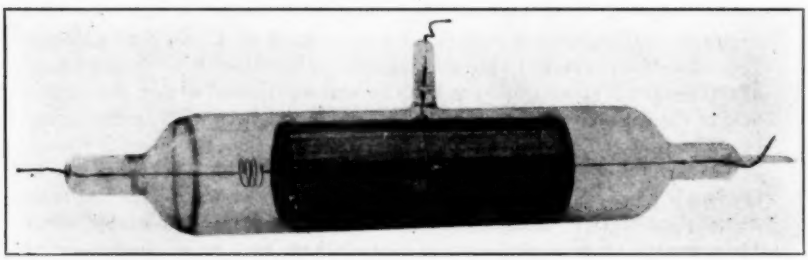

Fig. 1. Photograph of typical magnetron.

lows: (a) In the absence of magnetic field the electrons travel radially in straight lines, from cathode to anode (Fig. 2a). (b) A weak magnetic field parallel to the cathode curves their paths slightly, in planes normal to the cathode (Fig. 2b). (c) If the voltage between cathode and anode is kept constant the curvature of paths will increase with increasing magnetic field, and at a certain field strength the electrons will strike the anode almost tangentially (Fig. 2c). They will still all reach the

[1] Hull, Phys. Rev. **18**, 31-57, 1921; J.A.I.E.E. Sept., 1921, pp. 715-723. My attention has recently been called to the fact that H. Greinacher (Verh. D. Phys. Ges. **14**, 856, 1912) had previously suggested the use of such a tube for measuring e/m, and worked out part of the mathematical theory here given. His failure to obtain experimentally the predicted results was due to the combination of poor vacuum and insufficient electron emission.

anode, however, so that no change in current will be observed if the emission from the cathode is limited by its temperature, and only a slight decrease, due to the greater length of path of the electrons and correspondingly increased space charge, when the current is limited by voltage (space charge limitation). (d) A further increase in magnetic field causes

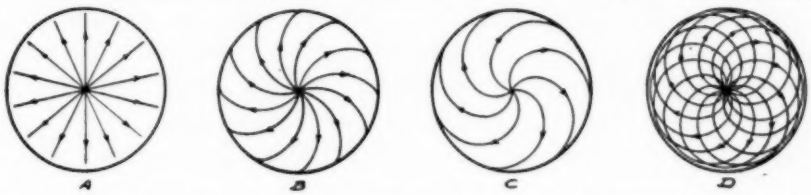

Fig. 2. Cross-section view of magnetron, showing effect of a magnetic field parallel to the axis on the paths of the electrons.

the electrons to miss the cylinder entirely and return to the cathode (Fig. 2d). The current to the anode falls abruptly to zero, in the case of perfect vacuum and perfect symmetry. Under practical conditions of vacuum and symmetry, an increase of about 10 per cent in magnetic field is required to reduce the current from its maximum value to essentially zero, and the reduction is not quite to zero, but to a small residual value corresponding to the number of electrons that are deflected from

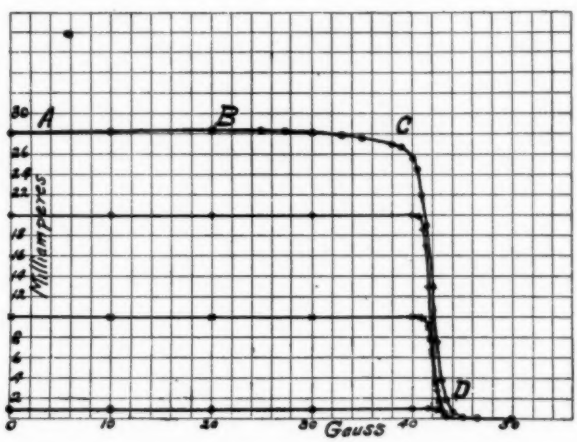

Fig. 3. Effect of magnetic field on current through magnetron. In the upper curve the current is limited by space-charge, in the other three by filament temp.

their paths by collision with gas molecules or unsymmetrical parts of the tube, and hence can be kept from the anode only by a magnetic field much stronger than the "critical" value. This residual current is of the order of a tenth of a milliampere at 250 volts, but may be as high as 50 milliamperes in good vacuum at 10000 volts. In using a magnetron to

measure magnetic field strength it is obviously necessary to use currents larger than this residual value.

An example of the electrical characteristics just described is shown in Fig. 3. The stages represented in Fig. 2 are designated by the corresponding letters A, B, C and D. In the upper curve the current is limited by space charge. In the lower ones it is limited by filament temperature. The portion c—d becomes more nearly vertical the higher the voltage and the more perfect the symmetry.

The critical value of magnetic field which is just sufficient to prevent electrons from reaching the cylinder is given[2] by the equation

$$H_0 = \sqrt{(8m/e)}V/R = 6.72V^{\frac{1}{2}}/R \qquad (1)$$

where R = radius of cylinder in cm;

V = potential difference between cathode and cylinder in volts;

H_0 = magnetic lines per cm^2 (gauss) parallel to axis of tube.

It is evident from Eq. (1) that for a given magnetron, H_0 is a function of voltage only.

Circuit and Operation

Method 1. Medium fields. For measuring fields of medium strength the simplest method of operation is that shown in Fig. 4. The cathode of the magnetron is connected to the negative terminal of a generator or other source of voltage E_0, and the anode is connected through a high resistance r to the positive terminal. The same source of voltage may be used to furnish heating current for the cathode, through a resistance r_1, as shown in Fig. 4, or a separate source of either direct or alternating

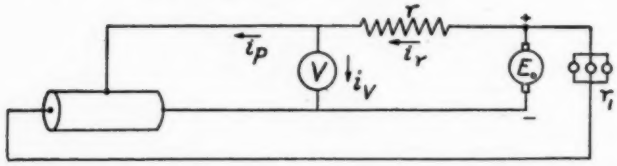

Fig. 4. Circuit for measuring magnetic fields between 20 and 500 gauss by means of magnetron.

current may be used. The temperature of the cathode is adjusted once for all at a value high enough so that under operating conditions the electron emission will never be limited by temperature. This adjustment is easily made in practice by gradually increasing the current through the filament until further increase has no effect on the voltmeter reading, and then adding about 10 per cent, e.g. by decreasing r_1 by 10 per cent, to allow for voltage fluctuation.

[2] Hull, Phys. Rev. **18**, 34, 1921.

A standard portable D. C. voltmeter V, preferably of low current type, is connected in multiple with the magnetron, and measures the potential between cathode and anode during operation.

The operation consists in placing the magnetron in the field to be measured, with its axis parallel to the direction of the field, if this is known, and reading the voltmeter. If the direction of the magnetic field is not known, the magnetron must be rotated until the voltmeter reading is a maximum. The direction of the field will then be given by the direction of the axis of the magnetron, and its magnitude by the voltmeter reading, by means of Eq. (1).

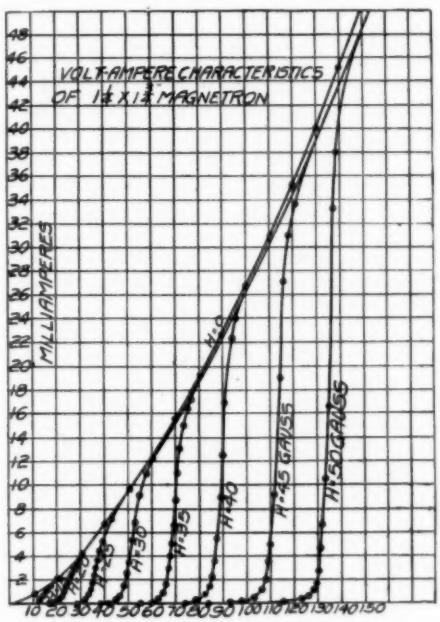

Fig. 5. Volt-ampere characteristics of magnetron for a series of values of magnetic field.

This relation is a theoretical one, and has been found to be reliable within the limit of accuracy of construction of the magnetron. The constant of the instrument, $6.72/R$, depends only on the radius R of the anode, assumed to be of circular section and concentric with the cathode. With ordinary care in construction, using the value of R measured either before or after assembly, this constant may be relied on within 5 per cent. The $V^{\frac{1}{2}}$ relation is exceedingly accurate over a narrow working range; so that for relative measurements, such as testing the uniformity of a field, the limit of accuracy is that of reading the voltmeter. An ordinary voltmeter may easily be read to $\frac{1}{2}$ per cent, making an accuracy of $\frac{1}{4}$

per cent in H; and with a precision voltmeter and constant voltage an accuracy of 1/20 per cent is attainable.

For a wide range of values of H there is a small systematic deviation from the $V^{\frac{1}{2}}$ relation when a fixed value of resistance r is used. This is due to the finite slope of the volt-ampere curves, as shown in Figs. 5 and 8. It may be avoided by varying r, as explained below, or may be allowed for by calibration.

The operation of the circuit shown in Fig. 4 is most easily described by reference to the volt-ampere diagrams shown in Figs. 5 to 8.

Fig. 5 shows a family of volt-ampere characteristics, for a series of values of magnetic field, of a magnetron with anode $1\frac{1}{4}$ inches in diameter and $1\frac{3}{4}$ inches long. The upper curve, marked $H=0$, gives the current when there is no magnetic field. This is the maximum current that can be obtained at the corresponding voltage. Its value is limited only by the space charge of the electrons, and is given accurately (except for end corrections) by the equation[3]

$$i(\text{amp.}) = 14.7 \times 10^{-6}(L/R)E^{3/2} \text{ (volts)}$$

where L and R are the length and radius of the cylinder. The family of curves marked 15, 20, 25 etc. represent the observed volt-ampere characteristics with constant magnetic fields of 15, 20, 25, etc., gauss respectively. It will be observed in each case that for voltages below a critical value the current is zero, and above the critical value it is practically the same as when there is no magnetic field. The critical voltages are less abrupt at low than at high voltage, because of the voltage drop along the filament. They are proportional to the square roots of the corresponding magnetic field strengths (cf. Eq. 1).

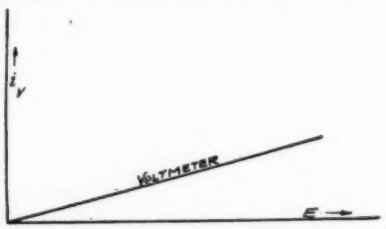

Fig. 6. Volt-ampere characteristic of voltmeter in Fig. 4.

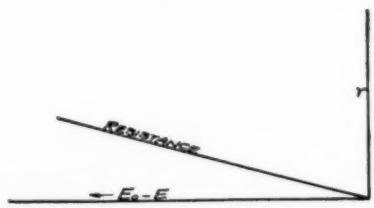

Fig. 7. Volt-ampere characteristic of series resistance in Fig. 4.

Figs. 6 and 7 show the volt-ampere characteristics of the voltmeter and the resistance r respectively. The abscissas in Fig. 7 are plotted to the left, in order that the graph may be inserted without change in Fig. 8.

Fig. 8 gives the complete volt-ampere representation of the circuit of Fig. 4. The family of curves marked "magnetron+voltmeter" are ob-

[3] Langmuir, Phys. Rev. **2**, 450, Dec. 1913.

tained by adding the ordinates of Figs. 5 and 6, and represent the volt-ampere characteristics of the multiple arc combination of magnetron and voltmeter. The curve marked "resistance" is the same as Fig. 7 with its origin placed at the point $E=E_0$ (E_0=generator voltage). The actual current and voltage for any magnetic field H is given by the intersection of the "resistance" curve with the "magnetron+voltmeter" curve for that value of H. This follows from the facts that the current i_r through the resistance r is equal to the sum of the currents i_p and i_V through the magnetron and voltmeter (Fig. 4), and the total voltage E_0 is the sum of the voltages across "magnetron+voltmeter" and "resistance."

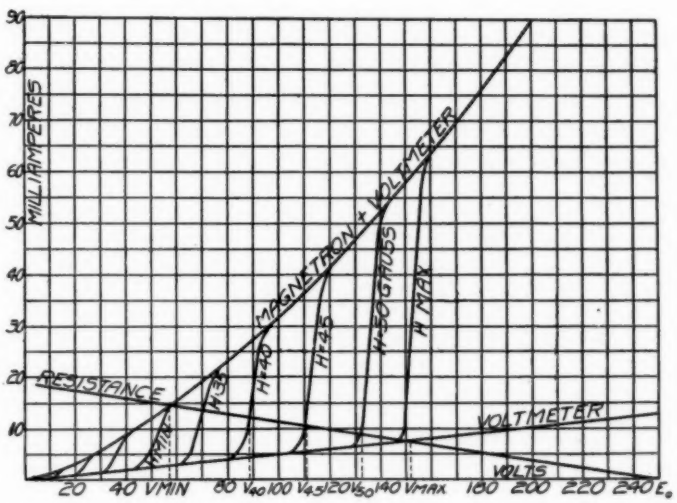

Fig. 8. Combined volt-ampere characteristic of circuit shown in Fig. 4. The voltmeter reading is given by the intersection of the curve marked "resistance" with that one of the "magnetron+voltmeter" curves which corresponds to the actual magnetic field.

It is evident from Fig. 8 that the voltages V_{40}, V_{45}, V_{50} etc. read by the voltmeter are the "critical" voltages for the corresponding magnetic fields,[4] and may therefore be used as a measure of the magnetic field, according to Eq. (1). This applies, of course, only to the range of magnetic field between H_{min} and H_{max}. For fields weaker than H_{min} the voltmeter reading is determined by space charge, and is independent of magnetic field, while for fields stronger than H_{max} the voltmeter reading is determined by the resistances of the voltmeter and series resistance r,

[4] The error due to the slope of the "critical" portions of these curves is discussed below. This error may be avoided by adjusting the resistance for each reading so that it intersects the vertical portion of the volt ampere curve at its middle point.

and is entirely independent of the magnetron. In practice it is easy to find these limits by observing once for all (for a given r and E_0) the voltmeter readings below which and above which the magnetic field has no effect, or by observing, in the absence of magnetic field, the values of voltmeter reading with magnetron filament lighted (lower limit, V_{min}) and not lighted (upper limit, V_{max}) respectively.

The range H_{min} to H_{max} may be adjusted to include any desired values of H, within wide limits, by changing the resistance r or the voltage E_0, as is evident from Fig. 8. The weakest field that can be measured is determined principally by the voltage drop in the filament, which makes the critical voltage indefinite at low anode voltages. For ordinary tubes this limit is about 20 gauss. The strongest field that can be measured is determined by the ability of the tube to operate on high voltage without evolution of gas. With ordinary tubes this upper limit is about 200 gauss, but a well evacuated tube of small anode diameter may measure as high as 500 gauss. It is to be noted that the magnetic field increases as the square root of the voltage, so that a 10 to 1 range of magnetic field requires a 100 to 1 range of voltage.

When the magnetron is operated as shown in Figs. 4 and 8 with fixed values of r and E_0, there is a small systematic variation from Eq. (1), due to the fact that the resistance curve does not cut the different magnetron curves at corresponding points, but near the top of the steep portion for weak fields, and near the bottom for strong fields (See Fig. 8). This error may be corrected by changing r or E_0 so as to make the tube current i_p increase uniformly with increasing V; or so that V is always in the middle of the range between V_{min} and V_{max}. The magnitude of this error and the degree of correction may be seen from Tables I, II and III.

The values in Table I are those obtained with constant voltage supply E_0 and constant series resistance r, using ordinary shop voltage for both

TABLE I

E_0 and r constant; $E_0 = 825$ volts; $r = 3600$ ohms

V (volts)	i_p (milliamp.)	H (gauss)	H (calc.) (gauss)
149	20.5	84	87
198	19.2	98	100
255		112	114
304	16.5	123	125
354		134	135
405	13.6	136	144
453		158	152
501	11.	176	160

V and H. From 85 to 150 volts, which is the operating range, there is a slow systematic deviation of the experimental values from about 2

per cent below the true value to 2 per cent above. The tube used in this test had an anode $\frac{3}{4}$ inch in diameter by $1\frac{1}{4}$ inches long.

Table II gives the values obtained with the same tube when the generator voltage is varied so that i_p is proportional to V. The values of $H=(6.72V^{\frac{1}{2}}/R)$ given by the magnetron agree with those of the calibrating coil (H, column 3) within the limit of constancy of the calibrating field, which was operated from shop voltages.

TABLE II

E_0 varied to make $i_p \propto V$

V (volts)	i_p (milliamp.)	H (gauss)	H (calc.) (gauss
25	1.25	38	36
50	2.5	51	51
100	5	72	72
200	10	101	101
400	20	143	143
600	30	176	175

Table III shows the degree of reliability of the readings obtained when an ordinary 250 volt shop supply is used for plate voltage, and the series resistance r is adjusted for each reading so that the reading is approximately in the middle of the "range" ($V_{min}-V_{max}$). The range was determined, for each value of r, by observing the voltmeter reading with

TABLE III

r varied to keep V in middle of "range"

V_{min} (volts)	V_{max} (volts)	V (volts)	H (calibrating coil) (gauss)	H (magnetron) (gauss)
11.0	18.0	14.0	15.7	15.8
13.3	21.2	16.5	16.9	17.1
14.5	24.0	19.7	18.83	18.75
16.3	27.8	22.0	19.75	19.81
18.5	32.2	25.3	21.25	21.26
21.3	38.6	29.4	22.80	22.90
25.5	47.5	34.6	24.40	24.81
32.0	61.0	45.7	28.43	28.6
44.5	89.0	65.5	33.95	34.2
58.0	114.	84.4	38.77	38.8
73	140	102.4	42.7	42.8
89	160	115.5	45.4	45.4
96	165	129.7	48.2	48.2
100	170	135.6	49.4	49.2

filament on and off respectively, with $H=0$. In this test the calibrating field was furnished by a long single layer solenoid 4 inches in diameter by 4 feet long, operated from storage batteries. The magnetron anode had

a diameter of $1\frac{1}{4}$ inches and a length of $1\frac{3}{4}$ inches. The voltmeter was a standard G. E. type DP_2 voltmeter, reading 150 volts full scale. Voltage was measured from the negative end of the filament. The series resistance r varied from 200,000 ohms for the lowest reading to 4000 ohms for the highest. It is seen that the values of H given by the voltmeter readings are very accurate over the whole range, the maximum error being only about 1 per cent.

This last method of operating the magnetron is very convenient. In measuring an unknown field the procedure is as follows: The magnetron is placed in the field, with its axis parallel to the estimated direction of the field, with filament lighted and maximum series resistance. The volt-

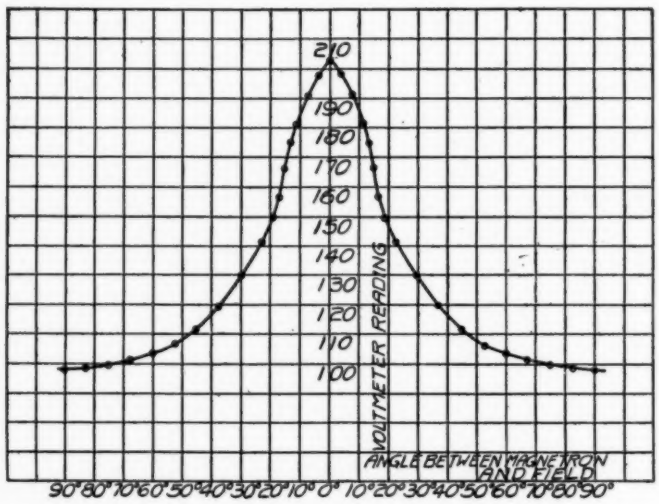

Fig. 9. Effect of the direction of magnetic field upon the reading of the voltmeter in method 1, using circuit shown in Fig. 4.

meter should read about 10 volts. As the resistance is gradually decreased, the voltmeter reading at first increases, then remains nearly constant over a certain range of resistance change, and then increases again. The range of voltage over which the voltmeter reading is approximately constant is the working range. The resistance is set at the approximate middle of this range, the tube is rotated about axes at right angles to its length until the voltmeter reading is a maximum, and this maximum reading is taken as a measure of the magnetic field. As a check the tube may be removed from the field (or the field annulled) and the resistance adjusted so that the voltmeter readings with filament lighted and not lighted respectively lie at equal distances below and above

the observed reading in the magnetic field. The tube should then be again placed in the field, rotated until the voltmeter reading is a maximum, and the final accurate reading observed.

The sensitiveness of the magnetron to direction of the resultant magnetic field may be seen from Fig. 9, which shows the effect of rotating the magnetron in a uniform magnetic field. The circuit is that represented in Fig. 4, with $E_0=250$ volts, $r=5400$ ohms, and a constant value of $H=102$ gauss. The ordinates are voltmeter readings of a 300 volt type DP_2 voltmeter in multiple with a $\frac{3}{4}$ inch diameter by $1\frac{1}{2}$ inch long magnetron. The abscissas are the angles between the axis of the magnetron and the magnetic field. It is seen that the voltmeter reading is a maximum when the axis of the magnetron is parallel to the field, and falls off rapidly as the axis is rotated, so that the direction of the field can easily be determined within one or two degrees. It will be noted that the decrease in voltmeter reading with angle is more rapid than the cosine of the angle at small angles and less rapid at large angles, i.e. the magnetron does not measure the *component* of magnetic field parallel to the axis, but only the *resultant* field when parallelism has been established.

Method 2. Weak fields. For measuring weak fields it is desirable to supply separately the ineffective part of the magnetic field (H_0, Fig. 3), by means of a constant current in a solenoid wound around the magnetron. The variation of plate current with magnetic field is then that corresponding to the steep portion ($c-d$, Fig. 3) of the $I-H$ curve, and it is possible to measure fields as weak as 1/10 gauss with an ordinary milliammeter, with an accuracy of about 1 per cent.

Since the polarizing field H_0 is large compared with the fields to be measured, it must be very constant if the *zero reading* is to be steady, and the anode voltage must likewise be constant. This is not difficult with a good storage battery for the filament, and either storage battery or dry cells for the anode. But there is a much simpler method of maintaining a steady zero, based on the fact that the equation of the zero point, which is the middle of the steep portion of the $(I-H)$ curve, is by Eq. (1)

$$H_0=k\ V^{\frac{1}{2}}$$

Hence, if the field H_0 is furnished by a current i_0, which is derived from the anode generator voltage V by means of a device that makes i_0 proportional to $V^{\frac{1}{2}}$, then $H_0 \propto i_0 \propto V^{\frac{1}{2}}$, which is the required relation; and the zero reading will be independent of fluctuations of V.

A satisfactory device for producing a current through the polarizing coil proportional to $V^{\frac{1}{2}}$ is a standard gas filled tungsten lamp connected in series with the coil. It happens that in these lamps the variation of resistance with temperature and the cooling effect of the gas cooperate

in such a way that the current through the lamp is accurately proportional to the square root of the voltage at its terminals, over a wide range of voltage. Fig. 10 A shows a logarithmic plot of the volt-ampere characteristic, between 50 and 130 volts, of a 125 volt, 75 watt Mazda C (gas-

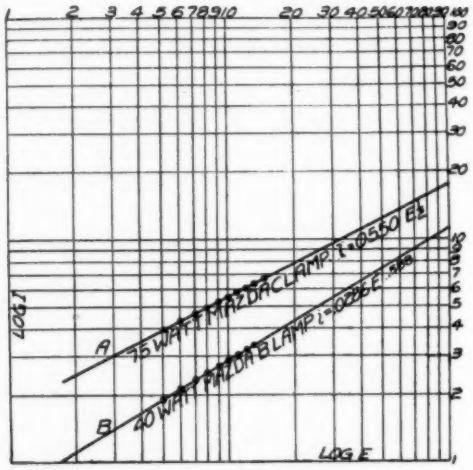

Fig. 10. A and B. Logarithmic plots of volt-ampere characteristic of Mazda C and Mazda B lamps, respectively.

filled) lamp. The points lie on a straight line whose slope is exactly $\frac{1}{2}$, representing the equation $i = .0550\ V^{\frac{1}{2}}$. Fig. 10 B shows a similar characteristic for a Mazda B lamp (vacuum type). The points again lie on a straight line, but its slope is .59, representing the equation $i = .0286\ V^{0.59}$. Hence the gas-filled lamp is a more perfect "regulator" for the

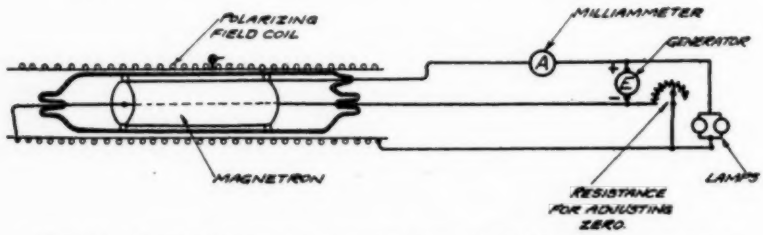

Fig. 11. Circuit for measuring weak magnetic fields with a magnetron.

current i_0 through the solenoid than the vacuum lamp. It is obvious that in order to utilize this regulating property of the tungsten lamp, the resistance of the field coil must be small compared with that of the lamp.

Fig. 11 shows the circuit for measuring weak fields, utilizing this resistance characteristic of a tungsten lamp in series with the polarizing

solenoid. For convenience, the solenoid is wound with such size of wire that it can be operated in series with the filament, furnishing the required heating current. The value of the current is fixed, once for all, to give the correct filament temperature, by the use of one or more standard 110 volt lamps in multiple. The number of turns of the solenoid is then adjusted so that this current produces approximately the required polarizing field (H_0, Fig. 3); and the final adjustment to exactly the right value is made by shunting the solenoid with a small variable resistance. The solenoid should have a length several times its diameter, so that the field inside the magnetron may be very nearly uniform.

A milliammeter, reading from 10 to 25 milliamperes at full scale, is connected in series with the anode. This milliammeter may conveniently by the same meter that is used as voltmeter in method 1, fitted with a "no resistance" binding post.

Curve I, Fig. 12, shows the calibration of a magnetron with anode $1\frac{1}{4}$ inches in diameter and $1\frac{3}{4}$ inches long, operated as shown in Fig. 11, from a 132 volt shop supply. The sensitiveness is approximately 15

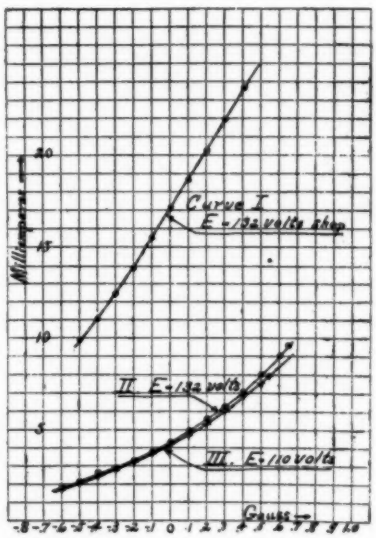

Fig. 12. Calibration curves of magnetron magnetometer for weak fields.

milliamperes per gauss. Curves II and III, Fig. 12, show two calibrations, of a magnetron, also $1\frac{1}{4}$ by $1\frac{3}{4}$ inches, at 110 and 132 volts respectively, with no change in the circuit constants. It is to be noted that the increase of voltage from 110 to 132 volts has increased the plate current uniformly by just 4 per cent over the whole range of magnetic field. This

example is given to show the degree to which this method of operation is independent of fluctuations in supply voltage. The voltage fluctuations which occur on standard supply lines are of the order of 5 volts or less, and it is seen that fluctuations of this magnitude would cause a variation of only 1 per cent in plate current.

Extension of range. The sensitiveness of method 2 may be reduced to any desired extent by inserting resistance in series with the anode. In this way the range may be adjusted to include any desired field from 1/100 gauss to 100 gauss. A convenient method of accomplishing this

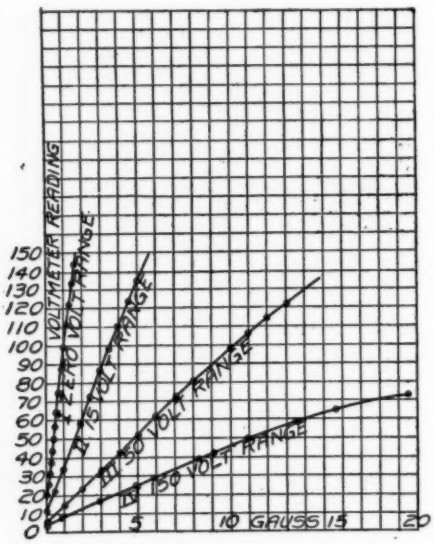

Fig. 13. Calibration curves of magnetron magnetometer, using circuit shown in Fig. 11, with different resistances in series with milliammeter to increase the range.

adjustment is to use as milliammeter a multiple scale voltmeter, which may be the same voltmeter used in method 1. Fig. 13 shows a series of calibrations taken with a standard type DP-2 voltmeter fitted with 4 scales, reading respectively 1/100, 15, 50, and 150 volts at full scale. It is seen that they cover satisfactorily the whole range from 1/100 to 20 gauss. In order to extend the range to 100 gauss with the same anode voltage, a magnetron with smaller anode diameter viz. $\frac{1}{4}$ inch, should be used. This would decrease the sensitiveness for weak fields. Conversely, the sensitiveness can be increased by the use of larger anode diameter.

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March 9, 1923.

A STUDY OF POLARIZATION CAPACITY AND RESISTANCE AT RADIO FREQUENCIES

By C. B. Jolliffe

Abstract

Polarization capacity and resistance of electrolytic cells having Au and Pt electrodes in H_2SO_4 solution, for frequencies of 11×10^4 to 2×10^6 cycles per second.—The cell was placed in a tuned circuit coupled to a generating circuit, and the polarization capacity C was computed from the change of capacity required to restore resonance as indicated by means of a second loosely coupled circuit containing a detector and galvanometer. The polarization resistance ΔR was obtained by substituting for the cell a variable non-inductive resistance. Both C and ΔR were found to be linear functions of $1/\sqrt{f}$ where f is the frequency. For Au electrodes, the curves all go through the origin but for Pt the limits for infinite frequency are positive for capacity and negative for resistance and vary with the concentration. For both Au and Pt the slopes of the capacity curves increase with concentration while the slopes of the resistance curves decrease. In the case of Au, $2\pi fC\Delta R=\tan\psi=\text{const.}$ (nearly), whereas for Pt, $\tan\psi$ varies. These results may be associated with the fact that the *residual current* is only 1/20 as much for Au as for Pt. *The effect of previous polarization* with H_2 is a temporary increase of capacity, while O_2 gives a permanent increase which cannot be removed by polarization with H_2. The roughness of the surface as well as the previous history affect the values of C and R obtained. Qualitatively the results for C and ψ are in agreement with the theory of Warburg, provided some assumptions are made, but not the results for ΔR. Possible reasons for the discrepancies are suggested.

Introduction

In 1860 Varley[1] noticed that two platinum electrodes immersed in a solution of sulphuric acid acted like a large condenser, and in 1871 he measured the capacity of such a cell by means of a ballistic galvanometer. A little later the behavior of such cells in an alternating current circuit was studied by Kohlrausch[2] who looked upon the capacity effect observed by Varley as due to polarization. He assumed that the e.m.f. of polarization was at any instant proportional to the total quantity of electricity that had passed through the cell, so that if E represents the e.m.f. then

$$E=\frac{1}{C}\int idt. \qquad (1)$$

[1] Varley, Phil. Trans. **161**, p. 129, 1871.
[2] Kohlrausch, Pogg. Ann. **148**, p. 143, 1873.

C has the dimensions of a capacity and has been called the "polarization capacity" or "electrolytic capacity" of the cell. The value of this factor has been measured by several experimentors by both direct and alternating current methods. A summary of the work done up to 1881 is given by Blondlot,[3] and up to 1897 by Gordon.[4]

It was found by Varley, Kohlrausch, Blondlot and others that the value of the polarization capacity was not constant for all voltages but increased as the voltage increased. Below a certain value depending on the solution, the capacity was however only slightly dependent on the voltage. Blondlot called the limiting value of the capacity as the voltage approached zero the "initial capacity." Bouty[5] and Vaillant[6] found that this initial capacity was proportional to the area of the electrodes.

M. Wien[7] studied the action of several kinds of electrolytic cells under the action of an alternating current supplied from an induction coil and measured both the initial capacity and the resistance. Assuming the relation of Kohlrausch and also as he did that the e.m.f. of polarization is 90° behind the current producing it, if an alternating e.m.f. $E_0 \sin \omega t$ is applied at the terminals of the cell,[8] then,

$$E_0 \sin \omega t = I_0[R \sin \omega t + (1/C\omega)\sin(\omega t - \pi/2)] \qquad (2)$$

where I_0 is the amplitude of the current produced, R the resistance, and $\omega = 2\pi$ times the frequency. Wien found that the measured resistance was always larger than the value computed from the constants of the cell. To account for this he assumed that there was a spontaneous depolarization at the electrodes which caused the polarization to reach its maximum earlier than it otherwise would. In Eq. (2) instead of $(1/C\omega)\sin(\omega t - \pi/2)$ he put $(1/C'\omega)\sin[\omega t - (\pi/2 - \psi)]$; then it becomes

$$E_0 \sin \omega t = I_0\{R\sin\omega t + (1/C'\omega)\sin[\omega t - (\pi/2 - \psi)]\} \qquad (3)$$

or

$$E\omega \sin\omega t = I_0[R + (1/C'\omega)\sin\psi]\sin\omega t + (I_0/C'\omega)\cos\psi\sin(wt - \pi/2). \qquad (4)$$

That is the resistance is increased by

$$\Delta R = (1/C'w) \sin \psi; \text{ and } C = C'/\cos\psi, \tan\psi = \Delta RC\omega. \qquad (5)$$

Wien studied the effects of frequency on the capacity and resistance between 64 and 535 cycles per second and found that C and ΔR decreased with frequency and that the product $\Delta RC\omega$ was nearly a constant.

[3] Blondlot, Jour. de Phys. p. 277, 1881.
[4] Gordon, Diss. Gött. **72**, 2nd paper.
[5] Bouty, Jour. de Phys. (3) **3**, p. 498, 1894; Comptes Rendus, **116**, p. 629.
[6] Vaillant, Comptes Rendus, **157**, p. 1141.
[7] Wien, Ann. der Phys. **294**, p. 37, 1896.
[8] Wien derived the equations with an applied e.m.f. of $E_0 \cos\omega t$. It has been changed in this paper to make the results consistent with later equations.

E. Warburg[9] proposed a theory to account for and determine the magnitude of the capacity from chemical data on the basis of diffusion of the products of electrolysis. He developed the relation that the e.m.f. to overcome polarization is

$$p=\frac{I_0}{sK\omega}\sin\phi\sin\left[\omega t-(\pi/2-\phi)\right],\ K=\frac{107.9}{AA'(\partial e/\partial\gamma)_0},\ s=\sqrt{\frac{k_1}{2\omega}}, \tag{6}$$

$$\tan\phi=1/(1+\mu/s), \tag{7}$$

where $$k_1=k\left(1+\frac{\gamma}{\gamma'}\sqrt{\frac{k'}{k}}\right)^2,\ \frac{\partial e}{\partial\gamma}=\frac{e-e_0}{\gamma-\gamma_0},\ \mu=\frac{\partial\Gamma}{\partial\gamma},$$

k and k' = diffusion coefficients of hydrogen into the solution and electrode; e and e_0 = e.m.f. at the surface of the electrode with and without current flowing; γ and γ_0 = density of hydrogen in solution with and without current flowing; A and A' = electrochemical equivalent of silver and of hydrogen; Γ = surface density of the hydrogen layer on the surface of the electrode.

From Eq. (3) it may be seen that the e.m.f. necessary to overcome that due to polarization is

$$p=(I_0/C'\omega)\sin[\omega t-(\pi/2-\psi)]. \tag{8}$$

Comparison of Eqs. (6) and (8) shows that

$$C'=sK/\sin\phi \tag{9}$$

where

$$C'=C\cos\psi,\ \tan\phi=\tan\psi. \tag{10}$$

Wien[10] tested the validity of these equations for palladium electrodes in sulphuric acid. He concluded that C and ψ are only slightly dependent on frequency.

The studies of polarization capacity that have been made heretofore have with one exception been made at frequencies in the audible range and with an induction coil as a source of alternating current. Merritt[11] using an electron tube generating set, measured the polarization capacity at frequencies in the audible range and also over a narrow band of radio frequencies. The object of the present work was to extend the range of radio frequencies and to measure the apparent resistance of the cell.

Method

The method used in this work was the same as that used by Merritt. The schematic diagram of connections is shown in Fig. 1. The coupling between the generating set and circuit A and also between A and B was

[9] Warburg, Non-polarizable electrodes: Ann. der Phys. **303**, p. 493, 1899; Verh. d. Phys. Ges. p. 120, 1896. Polarizable electrodes: Ann. der Phys. **311**, p. 125, 1901.

[10] Wien, Ann. der Phys. (4) **8**, p. 372, 1902.

[11] Merritt, Phys. Rev. **17**, p. 524, 1921.

always very loose in order to reduce as much as possible the reaction of one circuit on the other. The frequency was measured by means of a calibrated Signal Corps wave-meter (*SCR* 61) and was varied from 11×10^4 to 210×10^4 cycles per second. The detector used was a very sensitive molybdenite crystal which remained constant over a long period.

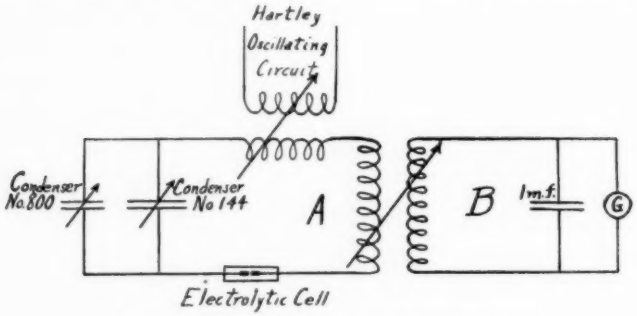

Fig. 1. Schematic diagram of circuits used.

The type of electrolytic cell used is shown diagrammatically in Fig. 2. The electrodes were made by sealing into glass tubing with DeKotinsky cement, rods of the metal used, 2 mm in diameter and 1 cm long, electrical connection being made by means of wires soldered to the rods and running through the tubing to the outside. The ends of the tubes were ground with emery so as to make the surface of the metal as nearly plane as possible. These tubes were then mounted by means of sealing

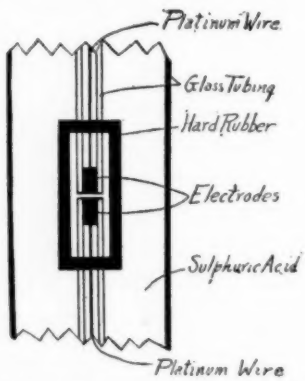

Fig. 2. Arrangement of the electrolytic cell.

wax in a hard rubber frame forming two parallel plates 2 mm in diameter and about 0.5 mm apart. This was mounted in a glass tube which contained the acid. The distance between electrodes was measured by means of a micrometer microscope. The cell so formed was linear, and a straight wire could be substituted for it without materially changing the

inductance of the circuit. Two of these cells were made, one having platinum electrodes and the other gold electrodes.

In order to measure the capacity of a cell the generating circuit was set for the frequency desired, the electrolytic cell being in circuit A. This circuit was then brought near the resonant frequency by adjustment of the inductance and the capacities to give maximum reading of the galvanometer G in the circuit C. To make the final adjustment for resonance, condenser No. 800 was fixed at a certain value and condenser No. 144, which had a small capacity, was varied until the circuit had passed through the resonance frequency. After this value for resonance was obtained accurately, the electrolytic cell was removed and in its place was put a piece of No. 40 B. and S. gauge Advance wire, the length of which was adjusted until the same current flowed at resonance as flowed with the cell in the circuit. This was indicated by the reading of the

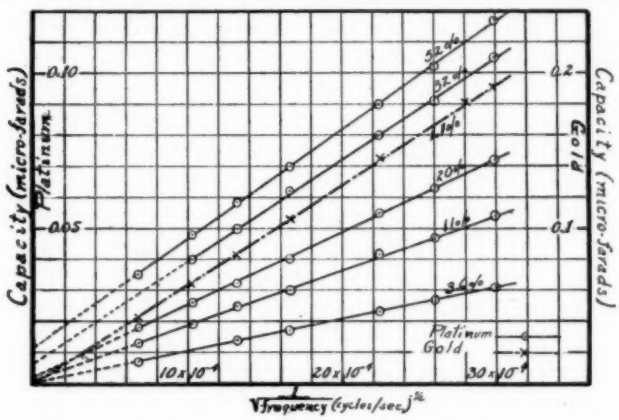

Fig. 3. Relation between capacity and frequency for different concentrations of H_2SO_4.

galvanometer being the same at resonance in both cases. The new value of the capacity required for resonance was obtained as before.

In order to be certain that the potential at the terminals of the cell was small enough so that the capacity could be considered as the initial capacity, the coupling between A and the generating circuit was changed so as to reduce the current in A. The capacities required for resonance were again determined with the cell and the resistance. The capacity reached a value which remained constant with further reduction in the current in circuit A. This was called the capacity of the cell and is the value plotted on the curves. The capacity of the electrolytic cell may be computed from the observed values of the capacity for the two resonance points. Since the current and phase relations of the circuit remained unaltered the resistance of the wire substituted is equal to the resistance of the cell.

The capacity measured was that corresponding to an equivalent air condenser so that this gave directly the angle ψ used by Warburg,

$$\tan \psi = \omega C(R - R_0) \tag{11}$$

where R_0 is the resistance of the cell as calculated from the dimensions and the conductivity of the acid.

Results

The results obtained are shown graphically in Figs. 3 to 6 inclusive. The observed values of capacity and $\Delta R = R - R_0$ are plotted as coordinates with $1/\sqrt{f}$ as abscissas where f is the frequency of the oscillations in cycles per second. The concentration of the sulphuric acid was varied over wide limits, the per cent of acid used in the solution in the cell being indicated on each of the curves. Within the limits of accuracy of the measurements all the curves are straight lines.

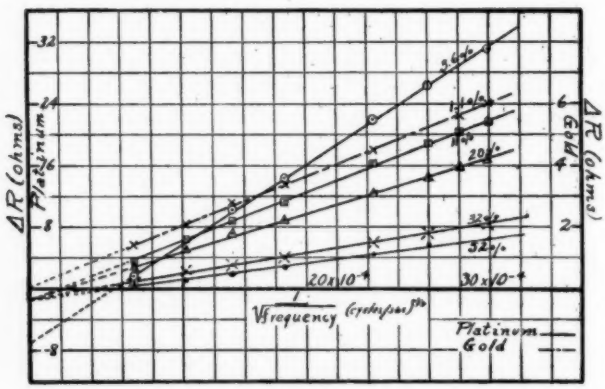

Fig. 4. Relation between ΔR and frequency for different concentrations of H_2SO_4.

For the curves of capacity and ΔR against $1/\sqrt{f}$ the straight lines when extended back pass through the origin when the gold electrodes were used but have intercepts on the capacity and resistance axes when the platinum electrodes were used. These intercepts are too large to be due to experimental errors and could be reproduced in every case.

When the curves shown in Figs. 3 and 4 were taken the electrodes had been exposed to the air for several weeks and at times this air was laden with fumes from a chemical laboratory. In order to bring the electrodes to a more standard condition the platinum was heated to about 1000°C and the gold to about 800°C in air in an electric furnace, and then a new cell made. This required that the surface be reground, and this time a glass plate with emery was used instead of a steel plate with emery as was used before. This gave entirely new surfaces, which were kept

immersed in the solution and only exposed to the air for a short time when the solution was changed.

Figs. 5 and 6 show the results after this treatment. The capacity and resistance show the same variations with frequency as before but the values are different as a result of the change in the character of the surface. It was found that these values could be decreased to one half by

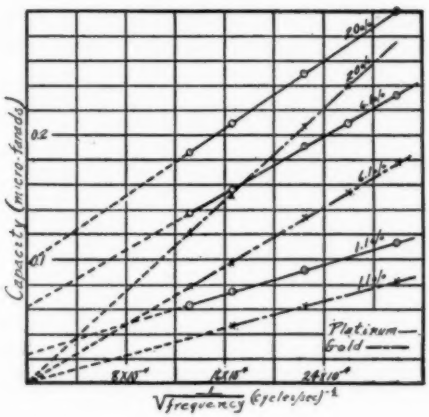

Fig. 5. Relation between capacity and frequency after new surfaces had been obtained.

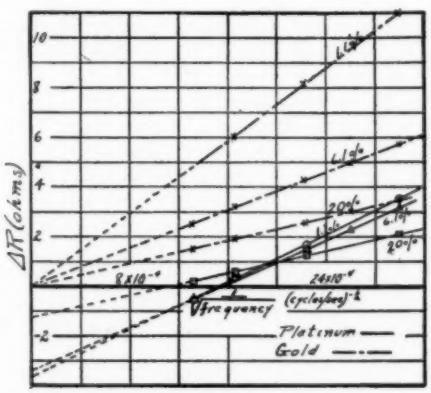

Fig. 6. Relation between resistance and frequency after new surfaces had been obtained.

polishing the surface somewhat instead of leaving it as it was after grinding it with the finest emery available (finishing emery).

For the platinum cell, $\tan \psi = \Delta RC\omega$ is a variable having both positive and negative values. For gold, $\tan \psi$ is a constant for each concentration and nearly constant for all concentrations both before and after heating. The value for ψ for all cases is between 30° and 40°.

It should be noted that the results obtained for capacity using platinum electrodes are different from the results of Merritt in that he found at radio frequencies that the polarization capacity varied inversely with f instead of inversely with $\sqrt{f}$. He found, however, that the square root relation was followed in the audible range of frequencies.

It was found by Scott[12] that when an electrolytic cell with platinum or gold electrodes was polarized, the capacity increased. In the method here used it was not practicable to keep the polarizing e.m.f. connected while measurements were being made. In order to polarize a cell both electrodes were connected together and to one pole of a dry cell. The other pole of the dry cell was connected to a platinum wire immersed in the solution. It was allowed to stand so connected for 24 hours and then was removed and measured as soon as possible. No bubbles of gas were visible.

Both the platinum and gold cells acted alike under this treatment. When the electrodes had been connected to the negative pole of the battery the capacity was initally doubled but decreased so rapidly that it was impossible to make accurate measurements. Within an hour it had decreased to the original value. The electrodes were then connected so that they were attached to the positive pole of the dry cell. When they were removed after 24 hours and measured the capacity was three times as great and this value was constant. It was measured three days later and had the same value. It was then connected again so that the electrodes were attached to the negative pole and allowed to stand. This caused the same temporary effect as before but the value to which it returned was the large value obtained after being connected to the positive pole. When the cell was taken apart and the electrodes examined it was found that they were considerably dulled. They were reground and when the surface was brought back as nearly as possible to the original condition the value of the capacity was found to have approximately its original value. From these results it appears that when the electrodes were polarized with hydrogen the increase was due to a temporary change in the solution or electrodes, possibly a change in the density of hydrogen, which soon returned to the original condition when the e.m.f. was removed. When the electrodes were polarized with oxygen, however, a permanent change was effected on the surface of the electrodes.

Comparison with Theory

In order to compare the results obtained with the theory of Warburg, Eqs. (7) and (9) may be solved for C and ΔR.

[12] Scott, Ann. der Phys. **303**, p. 388, 1899.

$$C = Ks[1 + s/(s+\mu)] + K\mu; \tag{12}$$

$$\Delta R = \frac{2s}{k_1 K} \cdot \frac{1}{(1+\mu/s)^2+1}; \quad \cot\psi = 1+\mu/s. \tag{13}$$

For the case of non-polarizable electrodes $\mu = 0$ and these equations reduce to

$$C = 2Ks; \ \Delta R = s/k_1 K; \ \tan\psi = 1. \tag{14}$$

The case of gold electrodes would seem to fall under the class of non-polarizable electrodes for the range of frequencies used except that tan ψ is not equal to unity. However the value of tan ψ is almost constant and does not differ much from unity. In the usual classification gold electrodes in sulphuric acid would not be classed as non-polarizable electrodes. It may be, however, that the value of μ is so small that it becomes of consequence only at higher frequencies than those used in this work.

For platinum electrodes the results for capacity would seem to agree with Eq. (12) for polarizable eiectrodes if it is assumed that μ is small in comparison with s. The results for ΔR do not agree with Eq. (13) for this equation does not allow a negative intercept on the resistance axis. The value of cot ψ for the platinum electrodes increases with decrease of s but becomes negative, which would not be allowed by Eq. (13).

In the light of these facts it may be concluded that through the frequency range used in this work, the theory of Warburg can only roughly explain the phenomenon both in the case of gold and platinum electrodes. However, further work is necessary before an entirely satisfactory quantitative test can be made. Further information might be obtained by extending the investigation to higher frequencies. The quantity μ should be investigated since even qualitative comparison of the results and the theory depends on the magnitude of this quantity. Warburg assumes that this quantity is a constant and that Γ is always in equilibrium with γ. At frequencies of the order used it is probable that this assumption is not justified and μ may be a function of frequency.

It has been assumed in this work as well as in the work of others that the electrolytic cell is equivalent to a capacity and a resistance in series and that $\Delta R = R - R_0$, where R_0 is calculated from the dimensions of the cell and the conductivity of the electrolyte. The fact that there is a "residual current" when the cell is charged with direct current would suggest that this is not a true representation. Possibly a truer assumption would be that the cell is a combination of two capacities in series with a resistance and this combination in parallel with a high resistance. Then $R - R_0$ would not give the ΔR required by Warburg's theory but

something smaller, and consequently a negative intercept might be expected when ΔR is plotted against $1/\sqrt{f}$.

To compare the residual current for the two kinds of cells, each cell was connected in series with a sensitive galvanometer and a variable direct e.m.f. The residual current is the value when the steady state has been reached. The following data were obtained for the residual current in scale divisions.

Voltage	*Residual current*	
	Platinum	*Gold*
0.1	4.7	0.0
0.2	7.0	0.2
0.3	9.4	0.3
0.4	13.5	0.4
0.5	15.0	0.7
0.6	17.0	1.0
0.7	25.0	1.3

This can be interpreted as indicating that the parallel resistance in the case of the cell formed by platinum electrodes is much smaller than in the case of the cell with gold electrodes. This may explain the lack of agreement of theory and experimental results in the case of the platinum electrodes.

In conclusion the writer wishes to express his thanks to Professor Ernest Merritt for his interest and suggestions concerning the work, and to Professor C. C. Murdock for the use of his bibliography on Electrolytic Capacity and for suggestions concerning the interpretation of the results.

PHYSICAL LABORATORY,
CORNELL UNIVERSITY,
January 27, 1923.

ACOUSTICAL POWER OF CERTAIN SOUND SOURCES IN ABSOLUTE UNITS

By Paul E. Sabine

Abstract

Acoustical power of certain sound sources in absolute units.—Having determined the threshold intensity (in absolute units) as a function of pitch for a particular observer (by Kranz' thermophone method) and the rate of dissipation of sound in the special sound chamber, the acoustic output of each of various sources in its fundamental or chief overtone, was computed from the observed duration of audibility of the sound after the source had ceased. The power of a *violoncello* in its fundamental when bowed strongly, varied from 1000 ergs/sec. at a frequency of 128/sec., to about 10 ergs/sec. at 650/sec., while a good *violin* gave a fairly uniform output of 600 ergs/sec. for frequencies from 192 to 1300/sec. An inferior violin gave a much lower output. Results are also reported for 23 *organ pipes*, from an open diapason stop, of pitches ranging from 129 to 3687 per sec. By introducing felt into the chamber to absorb the harmonies the acoustic power of the fundamental tone of a masculine *voice* was measured when intoning twelve different vowel sounds, at approximately the loudness of ordinary speech and at a frequency of 128. The output of the fundamental was found to be nearly the same for all these vowels, approximately 55 ergs/sec. Removing the felt, and fixing the attention upon the characteristic overtones of the vowels *ah*, *aw*, *ō* and *o͞o*, outputs of 225, 200, 32, and 10 ergs/sec. respectively, for these overtones were measured. Some observations for a feminine voice are also given.

Characteristic overtones of the vowels ah, aw, ō and o͞o.—The predominating overtone lies near a pitch characteristic of each vowel, varying little with the pitch of the fundamental. The pitches of these overtones for *ah*, *aw*, *ō* and *o͞o* were found to be 870, 460, 410 and 330, respectively. For a feminine voice, the pitch for *o͞o* rose from 258 to 326 as the loudness was increased to thrice conversational.

THE method of acoustical measurements developed by Professor Wallace C. Sabine[1] employs the threshold intensity for any pitch as the unit of sound intensity for that pitch.

In this system, intensity is measured as a density rather than as a flux. Thus the unit of sound energy is the energy in a cubic meter of barely audible sound. The power of a sound source is the number of cubic meters of barely audible sound emitted per second. Sound intensities are compared by comparing the times required for them to die away to threshold intensity within a closed space in which the rate of dissipation is known, this rate being determined in the first instance by comparing

[1] W. C. Sabine, Collected Papers on Acoustics, Harvard Univ. Press, 1922

the durations of audibility of sounds of known relative initial intensities.

No assumption is made as to the absolute value of the threshold intensity, nor as to the variation of this quantity with pitch. Further, the difference of the threshold intensity for a given pitch with different observers may be taken account of, so that observations made by different observers will yield the same results in measurements to which the method is applicable. The only assumption made is that the threshold of hearing for a given pitch and a given observer is a fairly definite and constant quantity. The consistency of the results of the method fully justify this assumption.

The extension of the method to problems in which absolute values are desired has awaited the adequate measurement of the absolute values of the threshold of audition for the entire range of tone. Earlier work on the latter problem gave widely varying results.[2] Moreover the recent work of Kranz[3] and of Fletcher and Wegel[4] shows that the variation of the sensitivity of the ear between different observers is great and that the difference of sensitivity for a slight difference of pitch for any one observer may also be large. However, the most recent work of Kranz[5] in this Laboratory, in which he employs a continuous pitch-variation at different levels of intensity, gives a complete curve of the threshold intensity in absolute units as a function of pitch, so that the threshold at any desired frequency is known without the uncertainty involved in interpolating between values obtained at discrete frequencies. The application of these absolute measurements to results obtained by Professor Sabine's Sound-Chamber Method in the determination of the acoustic power of various sources of sound furnishes the material of the present paper.

THEORY

Sound from a given constant source is produced continuously within an enclosure. It is at the same time being dissipated by absorption and finally reaches a steady state in which the rate of dissipation equals the rate of emission. If now the source ceases, the intensity of the residual sound decreases logarithmically.

Let E = acoustic power of source in ergs per second;

I = average intensity in ergs per cubic meter at any time t;

A = rate of decrease of intensity due to dissipation, defined by the equation $dI/dt = -AI$;

[2] Kranz, Phys. Rev. **17**, p. 384, 1921

[3] Kranz, Phys. Rev. **21**, p. 573, 1923

[4] Fletcher and Wegel, Phys. Rev. **19**, p. 553, 1922

[5] Kranz, Phys. Rev. **22**, p. 66, 1923

I_0 = intensity in the steady state;
i = threshold intensity in ergs per cubic meter;
J = threshold intensity measured in ergs per cm² per second;
V = volume of the room in cubic meters;
v = velocity of sound in meters per second;
a = absorbing power of room expressed in square meters of perfectly absorbing surface;
p = mean free path of sound between reflections;
s = total absorbing surface of the room;
t_1 = duration of audible sound after the source has ceased.

The general energy relation may be written at once:

$$E - VAI = V\, dI/dt \tag{1}$$

In the steady state, $I = I_0$, hence

$$E = VAI_0 \tag{2}$$

After the source has ceased

$$-AI = dI/dt \tag{3}$$

Integrating (3) and supplying the proper constants

$$\log (I_0/i) = At_1 \tag{4}$$

Substituting from (2)

$$\log (E/VAi) = At_1 \tag{5}$$

Now a/s = mean absorption coefficient, and v/p = number of reflections per second. Hence

$$A = (a/s)\ (v/p) \tag{6}$$

p the mean free path of a sound element between reflections may be shown to be equal to $4V/s$, hence

$$A = (a/s)\ (v/4v)\ s = av/4V \tag{7}$$

$$J \times 10^4/v = i \tag{8}$$

Substituting in (5) the values given in (6), (7) and (8) we have

$$\log_{10} E = vat_1/9.2V + \log_{10} (2500aJ) \tag{9}$$

In Fig. 1, the absorbing power, expressed in square meters of perfectly absorbing surface, for the Sound Chamber of this Laboratory in its standard condition, is plotted as a function of pitch, C_2 being 129 d.v. The values of a for the six C's were determined in the first instance by a method based on the times required for sounds of known relative intensities to die away to threshold intensity.

The value of J for any desired frequency was taken directly from the sensitivity curve of the more sensitive of the observer's two ears as determined by Dr. Kranz. From these data and the observed duration of audible sound after the source has ceased, the acoustic power of the source in absolute units is computed by means of equation (9).

The Power of Organ Pipes

The data from which the acoustic powers of these particular pipes were computed were not obtained in a single experiment for this specific purpose, but were taken from the notes of an investigation in the transmission of sound by standard walls which extended over a period of some six months. The time for each pipe is the average of nine sets of twenty-five observations each, these sets being taken at various times during this period. The average deviation of a single set from the mean of the nine sets, all for a single pipe, is 1.2 per cent. This variation indicates the degree of precision in the determination of the duration of audible sound. If it is assumed that this variation is due entirely to fluctuations in the acuteness of the observer's hearing, then this average

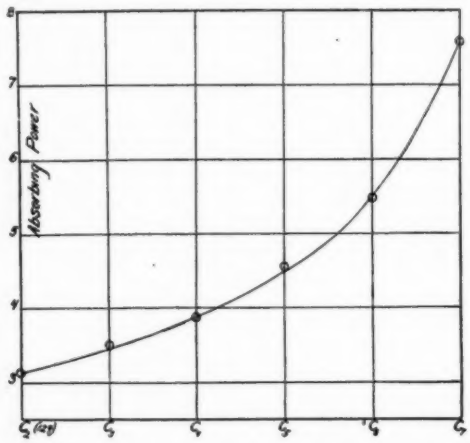

Fig. 1. Total absorbing power of sound chamber in square meters of perfectly absorbing surface

deviation of 1.2 per cent corresponds to a variation of approximately .09 in the logarithm of the threshold intensity, and an equal uncertainty in the computed values of the logarithm of the absolute power of the source of sound. The observational error in the determination of the threshold intensity is certainly as great as this, so that no great degree of precision can be claimed for the absolute values obtained by this method. However, in view of the great intrinsic difficulties involved in absolute acoustical measurements in general, it would appear that even roughly approximate values of the acoustic output of ordinary sound sources are desirable.

The logarithms of the power of the fundamental tone in ergs per second of twenty pipes ranging in pitch from 129 to 3100 d.v. are given by the small circles in Fig. 2. These were open diapason pipes, voiced to speak

at a pressure of $3\frac{3}{4}$ inches of water. The original voicing was done with a view to getting as nearly a pure tone as possible from each pipe rather than to securing a uniform loudness over the entire instrument. The diameters of the C_2 (129 d.v.) C_3, C_4 and C_5 pipes are 4, $2\frac{1}{2}$, $1\frac{3}{8}$ and 13/16 inches respectively. These dimensions are slightly greater than those given for the ordinary commercial "scale" in Wedgewood's Dictionary of Organ Stops. Doubtless the dimensions at the mouth of the pipe are a much more important factor in determining the power than is the diameter. The reaction of the stationary wave system set up in the Sound Chamber also may have a marked influence upon the speech of the pipe. This effect is largely eliminated by constantly shifting the stationary wave system by means of large steel reflectors that revolve slowly during the observations. The reflectors serve also to diminish effects due to the natural resonances of the room itself.

The large circles in Fig. 2 are the values computed from observations made by a second observer, whose sensitivity curve was markedly different from that of the first observer. The crosses are from observations

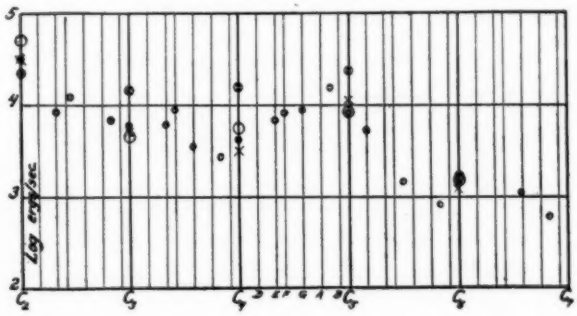

Fig. 2. Power of open diapason organ pipes. ○ As determined by first observer with sound chamber in standard condition. × By first observer, with sound chamber modified. ○ By second observer. ⊗ Second set of pipes voiced for higher blowing pressure.

made by the first observer with the absorbing power of the room increased by introducing a considerable area of absorbing material. The results indicate considerably more power in the lowest pipes and a marked decrease in the power of the pipes above C_5. Results of similar tests with the C pipes of another set made and voiced by a different manufacturer and speaking at a pressure of $5\frac{1}{4}$ inches are also given in Fig. 2, by crossed circles. The generally greater power of the more strongly winded pipes is to be noted, as well as the fact that the relative powers of the different pitches is approximately the same for the two sets.

Acoustical Power of the Violoncello and the Violin

The measurements with the violoncello were made with the assistance of Professor Karapetoff of Cornell University whose kind cooperation it is a pleasure to acknowledge, as well as the assistance of Mr. W. F. Friedman, in the tests of the violin.

Unfortunately the instrument used for the violoncello tests was a new instrument and its response was characterized by Professor Karapetoff as "very imperfect and sluggish." As yet, no opportunity for repeating the experiments with a better instrument has arisen. Points 1 of Fig. 3 give the output of this instrument when bowed for a uniform volume of tone, *forte* in musical notation, at the pitches indicated. All of the tones given are above the natural resonance of the body of air in the instrument

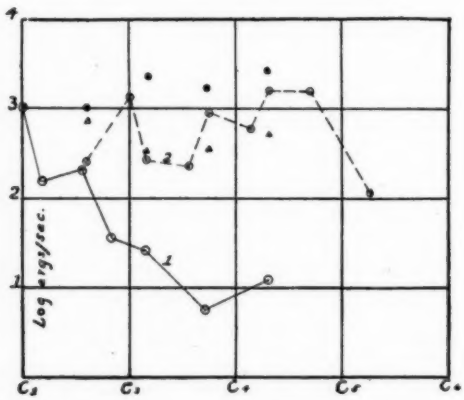

Fig. 3. 1. Violoncello bowed "forte." 2. Good violin bowed "forte." ● Good violin bowed for maximum tone. Δ Inferior violin, bowed for maximum tone.

which is in the neighborhood of G_1 (96 d.v.). The decrease of absolute power under bowing for uniform loudness with increasing pitch is what would be expected in view of the fact that the range of the instrument is that over which normal ears show an increase of sensitivity with rising pitch. The intensities of all the tones measured in terms of minimum audible intensity is surprisingly uniform over the entire range, suggesting that the skilled performer automatically regulates the bowing pressure at different pitches to allow for the varying sensitivity of the ear. Tests showed that *vibrato* tones had slightly less power than the same tones played with equal bowing pressure without the *vibrato*, and that the volume of tone from a string played "harmonically" was the same as that from the "stopped string."

Points 2 of Fig. 3 give the response in absolute units of a good violin played *forte* and bowed for equal loudness of all the tones. The conditions in the Sound Chamber were such as to absorb the harmonics more strongly than the fundamental, so that the values given are for the power of the latter, with the possible exception of the lowest tone. It was difficult to tell whether the most persistent tone in this case was the fundamental or the octave harmonic. An interesting comparison between two instruments is presented in the solid dots and the deltas of Fig. 4.

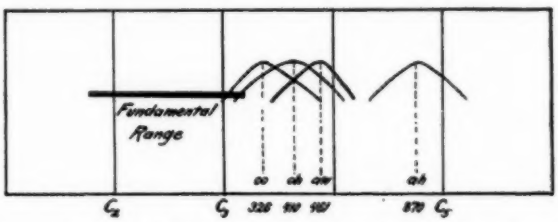

Fig. 4. Characteristic resonance regions for four vowel sounds

The first set was obtained with the violin used in the *forte* tests, the second with what Mr. Friedman called his "junk fiddle," an instrument whose history was unknown, the open strings of each instrument being bowed in succession for maximum tone.

The Absolute Power of Speech Sounds

The power of the human voice varies widely among individuals. Any attempt to determine what might be called an average voice would necessitate tests with a large number of voices, using a large number of syllables intoned over a considerable range of pitch by each voice. The recent work of Crandall and MacKenzie[6] on this problem, using fifty syllables spoken in a normally modulated voice by six different speakers (four men and two women), gives 125 ergs per second as the average acoustical output in connected speech. The present method is widely different from the telephonic method which they employed. However, results, so far as the order of magnitude of the acoustical output is concerned, are quite congruent with those obtained by them.

In the prolongation of a spoken or intoned syllable in a highly reverberant room, it is possible to pick out certain of the strong overtones which characterize a particular vowel sound. This is less difficult in the case of the vowels which Professor Miller has designated as of the first class, that is vowel sounds characterized by a single region of resonance, namely *ah*, *aw*, *ō*, *o͞o* (as in *moon*). With the aid of an observer who has

[6] Crandall and MacKenzie, Phys. Rev. **19**, 221, March, 1922.

a sense of absolute pitch it was possible to locate to the nearest semitone of the musical scale the particular overtones that predominated in each of these vowels. When the vowel sound is intoned, the exact pitch of the predominating overtones varies over a small range with varying pitch of the fundamental. They are in every case one or more harmonics of the fundamental but the particular harmonics for a given vowel lie within a narrow range of frequency characteristic of that vowel. This is illustrated below in the case of the vowel *ah*.

Pitch of Fundamental	*Pitch of Strongest Harmonic*	*Number of the Harmonic*
A_1 (109 d.v.)	A_4	8
B_1,	F_4	6
C_2 (129 d.v.)	G_4	6
D_2	F_4 *sharp*	5
	A_4	6
E_2	G_4 *sharp*	5
F_2	F_4	4
	A_4	5
G_2	G_4	4

In this way, the characteristic region of resonance for each of the four vowel sounds mentioned was determined by singing each of them successively at the intervals of the scale from A_1 (109 d.v.) to D_3 (290 d.v.). The results are plotted in Fig. 4, the ordinate for each frequency being fixed by the number of times that frequency was observed, and its relative prominence.

With the Sound Chamber in its standard condition, these characteristic overtones persisted longer than did the fundamentals. Thus it was possible to measure in absolute units the power of these overtones, as already described. With a little practice one can produce tones at a given pitch of remarkably constant loudness as measured by the time of reverberation. In order to determine the power in the fundamental, eight square yards of hair felt was brought into the Sound Chamber. This material absorbs sound of pitch above middle *C* much more strongly than below this so that in this condition it was the fundamental that persisted longest in each case. Thus the power in both the fundamental and the characteristic resonance region could be measured. The values obtained for these syllables intoned by a single voice at the pitch C_2 (129 d.v.) at the loudness of telephone conversation are given below.

POWER OF MASCULINE VOICE AT CONVERSATIONAL LOUDNESS

	ah	*aw*	*ō*	*o͞o*	
Fundamental (129 d.v.)	46	56	66	60	ergs/sec
Characteristic overtone	225	200	32	10	"
Total power	271	256	98	70	"

Tests conducted in the felted Sound Chamber using the twelve vowel sounds as in the words *father, tape, ten, team, term, tip, time, tone, ton, for, pull, rule,* gave a very nearly uniform power of approximately 56 ergs per second in the fundamental tone C_2 (129 d.v.) of this same voice at conversational loudness.

Less extensive tests on the feminine voice were made through the kind assistance of Miss Louise Wallace Hackney of New York. The vowels *ah* and *o͞o* were intoned at three levels of loudness. The speaker was asked to intone these vowels first at conversational loudness, then as if addressing a small audience, and finally in the tone that would be used in addressing a very large audience. It was interesting to note that the increasing loudness in the vowel sound *o͞o* was accompanied by a rise in pitch of two whole tones, whereas for the vowel *ah*, there was a barely perceptible pitch change. The natural pitch of the speaker's conversational voice was close to C_3 (258 d.v.) very near the characteristic pitch of the vowel *oo*. Raising the pitch would thus bring the fundamental frequency into unison with the resonance frequency of the vocal cavity as formed for this vowel thus increasing the power of the sound. This is apparently what the speaker did, either unconsciously or as a result of training. It is also significant that this rise in pitch on the vowel *o͞o* increases the audibility of the sound because of the increased sensitivity of the ear with a rise of pitch in this region of the scale. Neither of these effects would follow from raising the pitch of *ah*, since the characteristic is almost two octaves above the fundamental of this particular voice, and in a region where the sensitivity of the ear does not vary markedly with pitch. Measured in terms of minimum audibility the change from conversational to the loud speaking voice was by a factor of about twelve for both vowels, whereas the change in absolute power for *o͞o* was by a factor of only three, as shown below.

POWER OF A FEMININE VOICE

	Conversational	*Small audience*	*Large audience*
Characteristic harmonic of *ah*	40 ergs/sec.	145 ergs/sec.	510 ergs/sec.
Fundamental of *o͞o*	16 (258/sec.)	21 (290/sec.)	46 (326/sec.)

In the paper by Crandall and MacKenzie already referred to, the authors give curves showing the energy distribution in speech as a function of pitch, and note that the distribution deduced by their method gives a greater portion of the total energy in the fundamentals than is indicated by a similar curve synthesized from the harmonic analysis of vowel sounds as given by Professor Dayton C. Miller. Their curves indicate that the larger proportion of the energy in speech is below 500/sec.

whereas Miller's results (according to Crandall's and MacKenzie's analysis) point to the range between 500 and 1000/sec. The results of the present experiments place about 70 per cent of the energy of the four vowels of the first class intoned by this particular masculine voice in the frequency range below 500/sec. Doubtless variations among individuals in this regard are as great as in the total output of voices. Observations of individual speaking voices certainly show wide differences in the relative strengths of the fundamental and the characteristic partial tones. Inspection of the individual distribution curves given in Crandall and MacKenzie's paper confirm this observation. Doubtless also, the difference in the characteristic resonance region of the vowel sound *aw* as given by Miller from that given in the present paper are to be ascribed to individual peculiarities of the speakers.

RIVERBANK LABORATORIES,
GENEVA, ILLINOIS,
March 16, 1923.